GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

REVISED

no action
ADS

Date: October 21, 1976 OHL

Project Title: Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethanes

Project No: E-16-687

Project Director: Dr. Ben T. Zinn

Sponsor: Products Research Committee; The Society of the Plastics Industry, Inc.

Agreement Period: From 10/1/76 Until 10/1/77

Type Agreement: Contract (RP-75-1-15 Revised) dated 9/9/76

Amount: $30,000

Reports Required: Quarterly Progress Reports; Final Report

Sponsor Contact Person (s):

Technical Matters	Contractual Matters (thru OCA)
	Lowell R. Perkins Executive Director Products Research Committee c/o John W. Lyons Bldg. 225, Room B-142 National Bureau of Standards Washington, D.C. 20234

Defense Priority Rating: None

Assigned to: Aerospace Engineering (School/Laboratory)

COPIES TO:

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- Project Code (GTRI)
- Other

CA—3 (3/76)

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

no action 8/78

Date: 1/18/78 OK

Project Title: Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethanes.

Project No: E-16-687

Project Director: B. T. Zinn

Sponsor: Products Research Committee, Society for the Plastics Industry, Inc.

Effective Termination Date: 10/1/77

Clearance of Accounting Charges: 10/1/77

Grant/Contract Closeout Actions Remaining:

- X Final Invoice and Closing Documents
- _ Final Fiscal Report
- _ Final Report of Inventions
- _ Govt. Property Inventory & Related Certificate
- _ Classified Material Certificate
- _ Other _____

Assigned to: Aerospace Engineering (School/Laboratory)

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CA—4 (3/76)

PRODUCTS RESEARCH COMMITTEE

RESEARCH PROJECT NUMBER [RP-75-1-15 Revised]

INVESTIGATION OF THE PROPERTIES OF THE COMBUSTION PRODUCTS GENERATED BY FIRE-RETARDED POLYURETHANES

Quarterly Progress Report

for the period

October 1, 1976 to December 31, 1976

CO-Principal Investigators: Dr. B. T. Zinn, Regents' Professor

Dr. R. A. Cassanova, Research Engineer

Other Personnel: Dr. E. A. Powell, Assistant Professor

Dr. C. P. Bankston, Research Engineer

Dr. J. U. Rhee, Assistant Research Engineer

Dr. S. N. Tsoukalas, Senior Research Chemist

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia

INTRODUCTION

This quarterly report describes the efforts conducted under Products Research Committee research project number [RP-75-1-15-revised] during the period October 1, 1976 to December 31, 1976. The grant under consideration is entitled "Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethane."

COMPOSITION OF SAMPLES

A series of tests has been conducted to determine the physical properties of the smoke produced during the burning of polyurethane samples specifically prepared for testing purposes by one of the leading chemical manufacturers. The chemical compositions of these samples are listed in Table I of this report. Testing with samples of known compositions will open the possibility of relating the measured physical and chemical characteristics of the smoke particulates to the presence of a particular additive in the test sample. Future plans call for testing of polyurethane samples that will be obtained from the sample bank which was established by the PRC and NBS. In this connection, an effort will be made to investigate the properties of samples used in toxicological tests and contacts have been established with Dr. Alarie from Pittsburgh in order to coordinate the choice of samples that will be utilized by both groups. Such cooperation will provide an opportunity for correlating the results obtained under the Georgia Tech program with those obtained by Dr. Alarie. Hopefully, such conditions will be effective in identifying the causes of the observed toxicological symptoms.

SUMMARY OF PHYSICAL PROPERTY MEASUREMENTS

A series of room temperature tests have been conducted in order to make an initial determination of the characteristics of the smoke produced during smoldering combustion of each of the five previously described samples.

TABLE I.

FLEXIBLE POLYURETHANE FOAM

FORMULATIONS - PARTS BY WEIGHT

COMPOSITION	A	B	C	D	E
Poly-G® 3030 PG	100.0	100.0	100.0	100.0	100.0
TDI 80	51.3	51.3	51.3	51.3	51.3
Water	4.0	4.0	4.0	4.0	4.0
Thermolin® 101	-	8.0	-	-	-
HB-32	-	-	8.0	-	-
FR-2	-	-	-	-	8.0
2XC20	-	-	-	8.0	-
L-5710	1.0	1.0	1.0	1.0	1.0
-C-2	0.250	0.250	0.250	0.225	0.225
Dabco 33 LV	0.300	0.300	0.300	0.300	0.300

CHEMICALS

Olin Poly-G® 3030 PG	is Glycerin propoxylated to a molecular weight of about 3000.
Olin TDI-80	is a mixture of 80% 2,4 and 20% 2,6 toluene diisocyanate.
Union Carbide L-5710	is a dimethyl siloxane polymer with Si-C-O linkages - also contains ethylene oxide-propylene oxide co-polyethers.
Air Products Dabco 33 LV	is 33% Triethylene diamine and 67% dipropylene glycol
Witco C-2	is Stannous Octoate

TABLE I continued

COMMERCIAL NON-REACTIVE

FLAME RETARDANTS

Manufacturer & Name	Chemical Compound	% Analysis P	Cl	Br
Monsanto 2XC20	Chlorinated Diphosphate Ester	10.6	35.2	-
Stauffer FR 2	Tris(2,3 Dichloro Propyl) Phosphate	7.2	49.1	-
Stauffer HB 32	Tris (2,3 Dibromo Propyl) Phosphate	4.5	-	68.7
Olin Thermolin^{R} 101	Tetrakis (2-chloro ethyl) ethylene diphosphate	13.0	31.0	-

Figure 1 shows the weight loss data and indicates that all five samples lose 70 to 80% of their initial weight in the first four minutes of exposure to a 5 W/cm^2 radiant heating level. However, compositions C and D left a slightly higher percentage of the initial weight as a char than did the other compositions.

Smoke particle size distributions which were obtained with the cascade impactor are shown in Figure 2 and 3. This instrument furnishes the distribution of particulate weight over the aerodynamic size range of 0.43 to 11 microns. The smoke is sampled continuously over the entire test time; thus, the resulting size distribution is an integrated distribution for the entire test. This type of data also gives an indication of the total particulate matter generated by each sample. The data shows that there are some differences amongst the five samples in the total particulate weight which is produced by a given sample. Composition A, which is the non fire-retarded sample, produced a greater concentration of larger particles and composition E produced a slightly lower concentration of smaller particles than the other compositions.

An indication of the time variation of the average smoke particle size during the tests is shown in Figures 4 and 5. Compositions A and E produced considerably larger particles in the early portion of the test than did the other three compositions. This trend is consistent with the cascade impactor data which was previously described.

Any variation in the particle concentration and size distribution will also cause noticeable changes in the smoke optical density. These comparisons are shown in Figures 6 and 7. The most noticeable result of this data is that the non fire-retarded sample, composition A, produced a higher optical density at a somewhat later time in the test than did the other

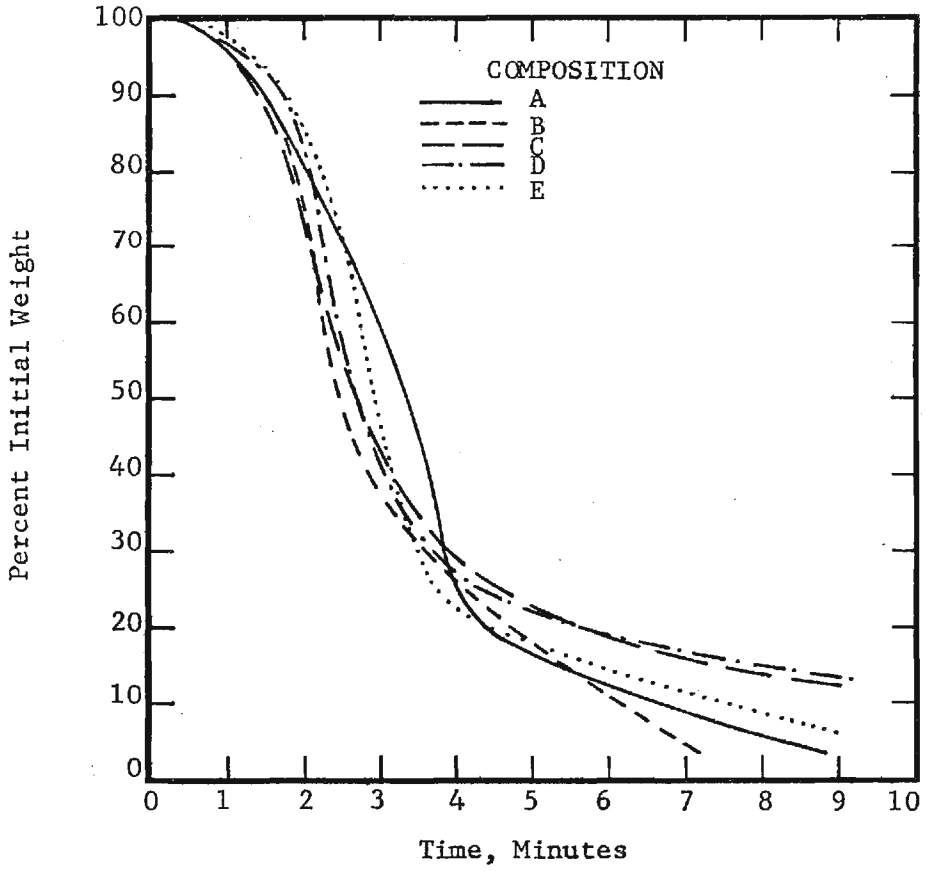

Figure 1. Weight loss of Polyurethanes During Smoldering Combustion at 5 W/cm^2 Radiant Heating in Room Temperature Air

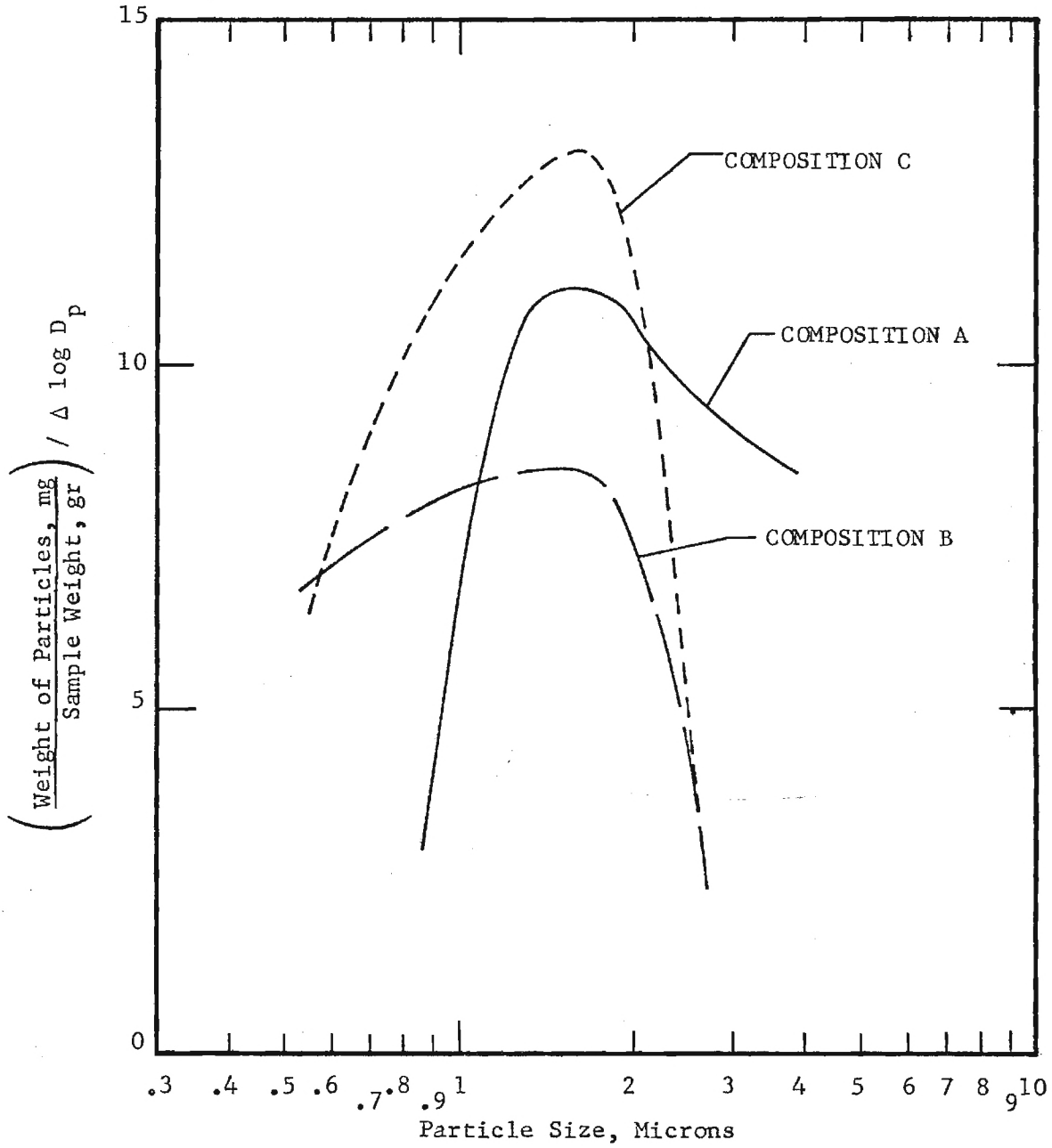

Figure 2. Smoke Particle Size Distribution Integrated Over the Entire Test Time - Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

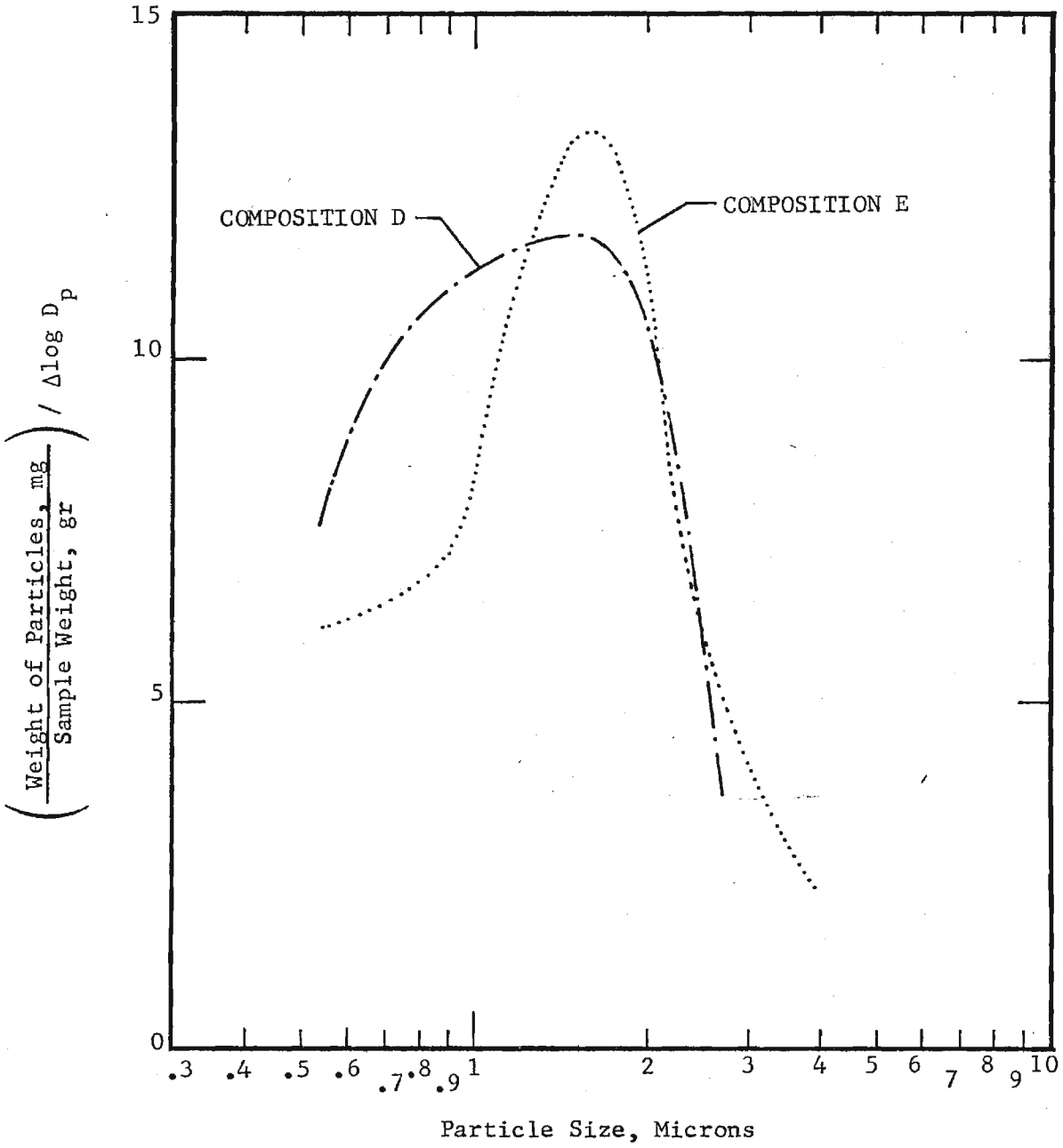

Figure 3. Smoke Particle Size Distribution Integrated Over the Entire Test Time - Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

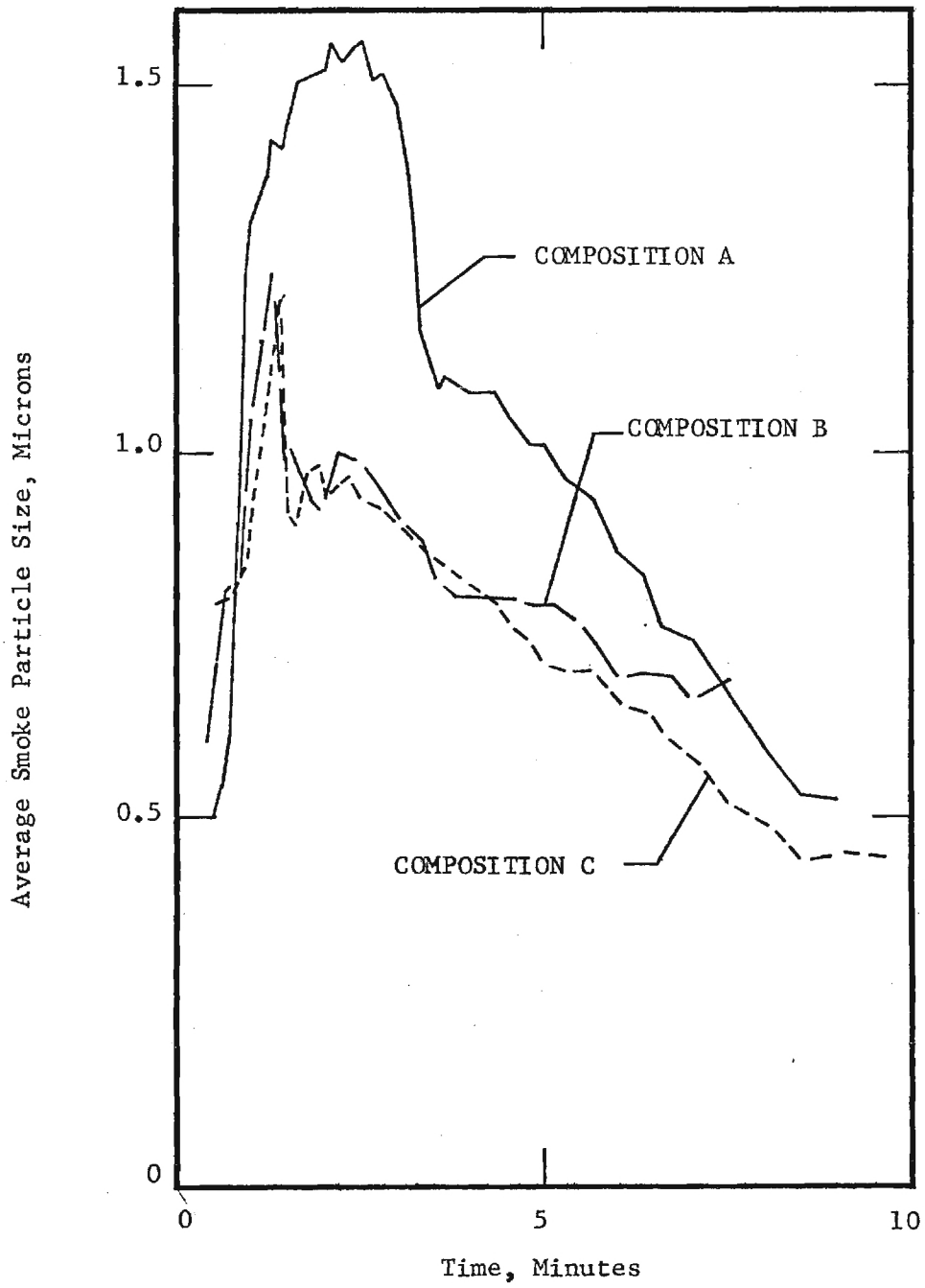

Figure 4. Average Smoke Particle Size Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

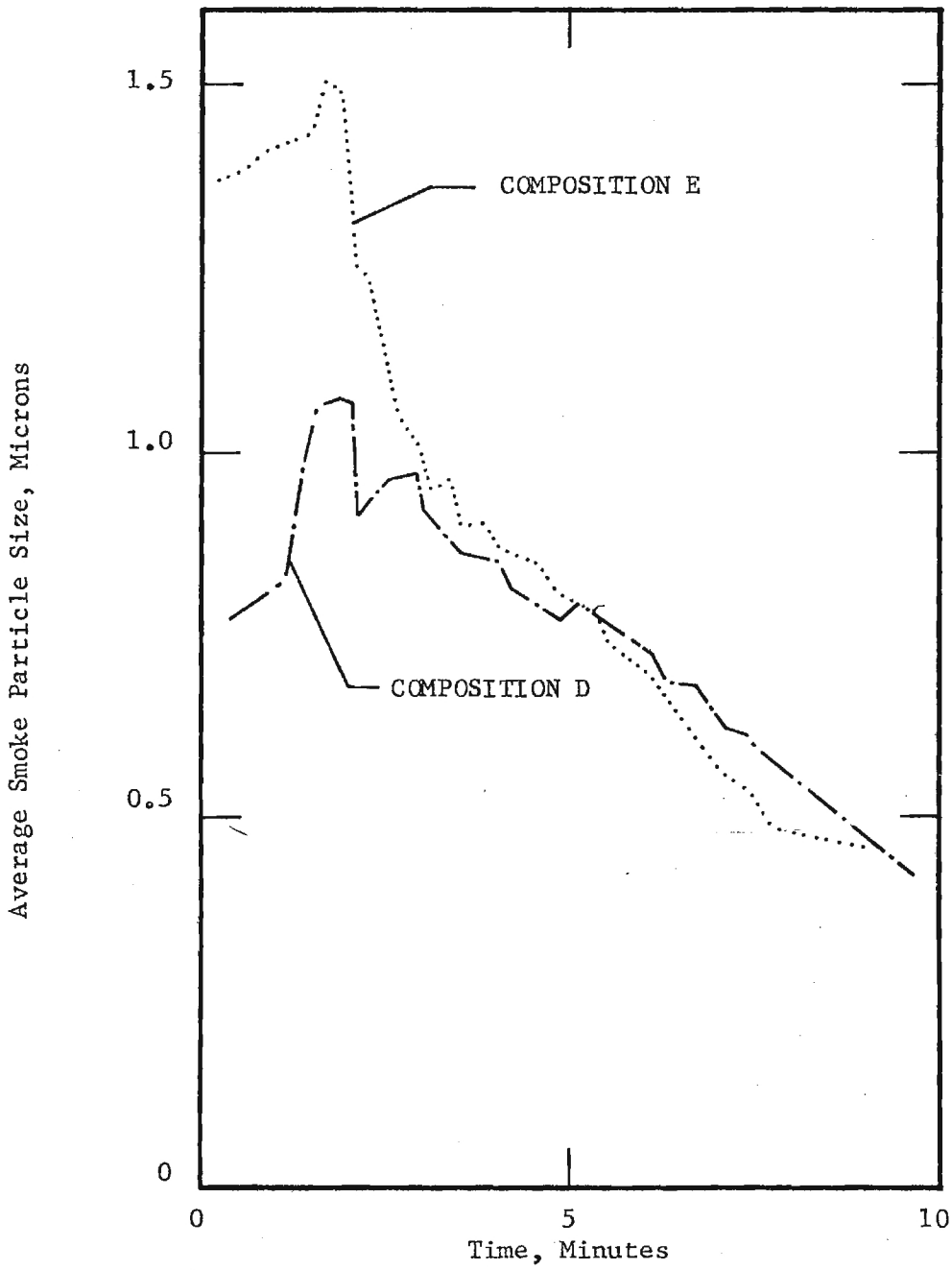

Figure 5. Average Smoke Particle Size Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

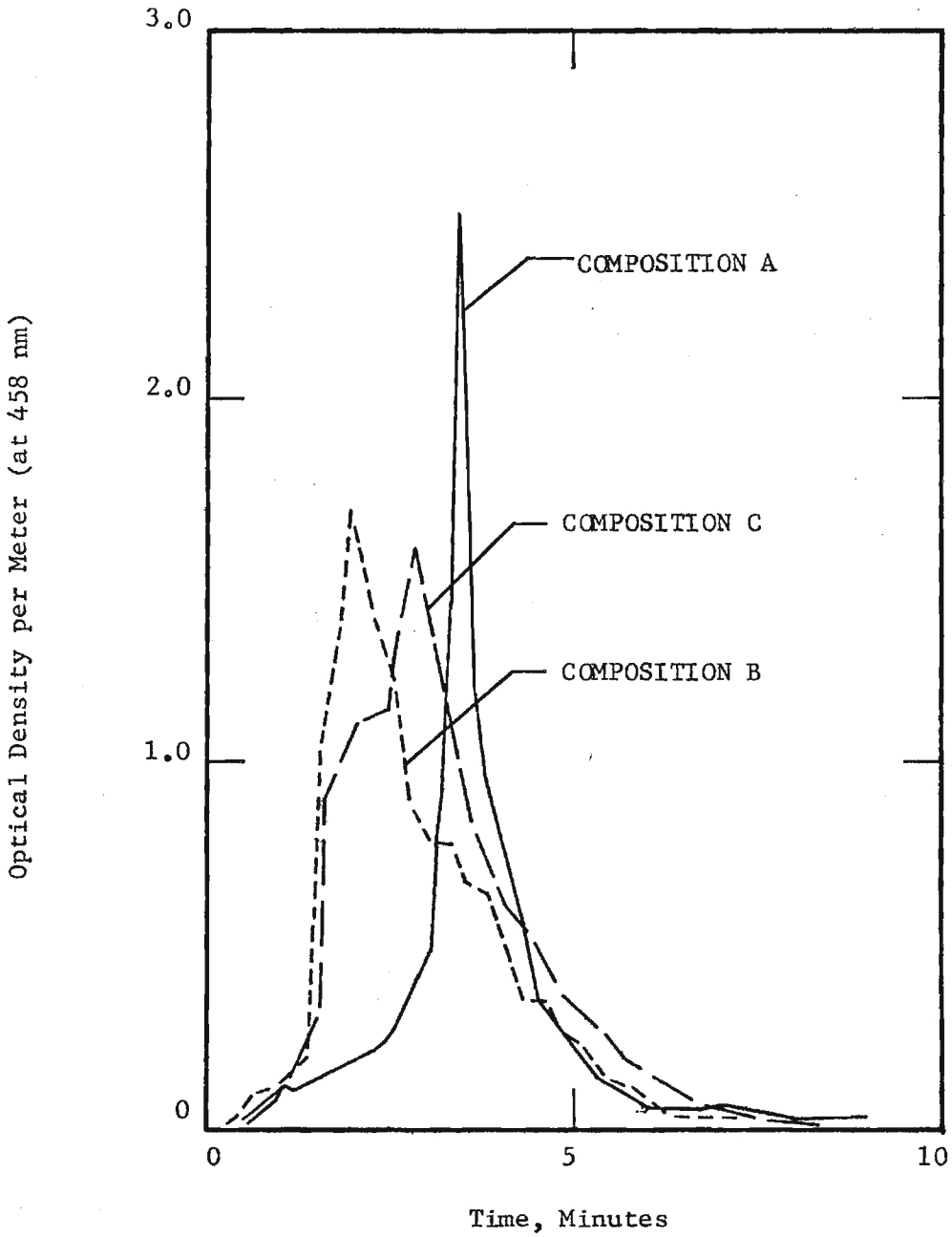

Figure 6. Smoke Optical Density Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

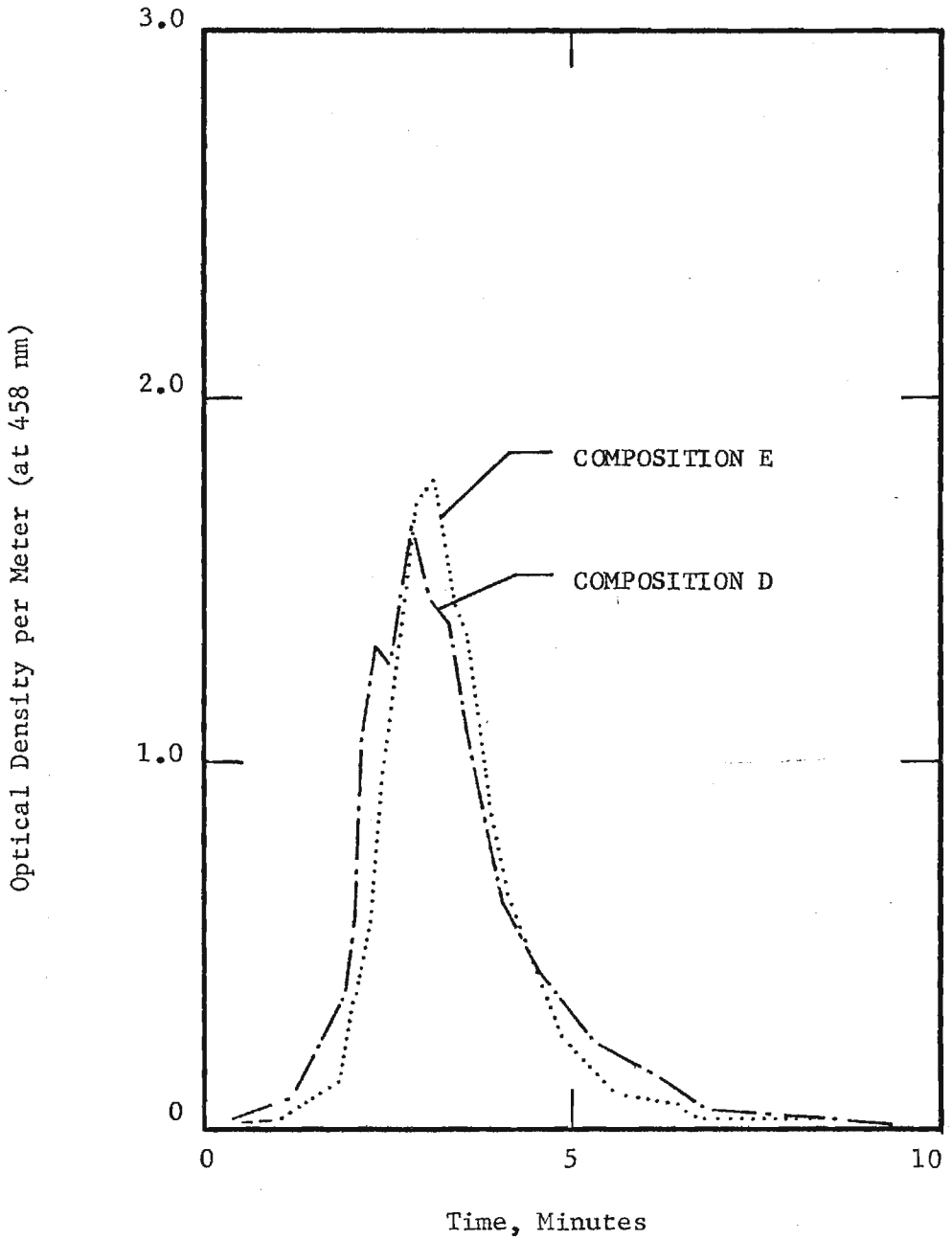

Figure 7. Smoke Optical Density Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

compositions. This greater optical density for composition A is consistent with the larger average particle size which was measured for this composition.

COMPUTERIZED DATA REDUCTION SYSTEM

During the report period a new mini-computer-based data reduction system was developed. This system consists of a Preston GMAD-11 analog-to-digital converter (ADC), a Hewlett Packard frequency synthesizer, an HP 2100S mini-computer and an HP 7901 disk mass storage system. As shown in Figure 8 the signals from the smoke monitoring instrumentation are first amplified or attenuated to accommodate the 0 to 2.56 volt range of the ADC. The signals are then sampled essentially simultaneously by sample-and-hold modules in the ADC. A multiplexer sequentially takes the data from the sample-and-hold modules where the voltages are converted to digital form and stored in the computer. The frequency synthesizer controls the sampling rate and is also used to time the experiment. Several hundred samples per second are taken, and the voltages from each of the instruments are averaged over one-second intervals. Because of the large number of samples taken during a test, the data are periodically read onto the disk, which serves as auxiliary storage.

Upon completion of a test, the data are reduced as illustrated in Figure 9 and plotted on a Zeta plotter. To avoid extensive data reduction times, the raw signals from the Laser system are first displayed on a Tektronix 4012 Graphics CRT. Selected points are taken and reduced to obtain plots of volume concentration, refractive index, and mean particle size versus time.

CHEMICAL ANALYSIS SCHEME FOR PARTICULATES FROM COMBUSTION OF POLYURETHANES

The very complex nature of the organic compound mix produced during the combustion of polyurethanes, and collected as particulates, requires a detailed analytical scheme. Specifically, it is essential to obtain a thorough separation of the many aliphatic and aromatic compounds present before a formal identification is attempted. Preliminary studies with organic extracts of particulates collected after combustion of polyurethanes have shown a very complex gas chromatographic pattern as shown in Figure 10, with many unresolved or partly resolved peaks. It is clear that simple gas chromatography alone, or even gas chromatography in conjunction with a chemical scheme of pre-separation will not improve the resolution of the gas chromatographic system sufficiently to present single compounds to the mass spectrometer. This will leave a degree of ambiguity in any interpretation of mass spectral data.

In order to overcome this limitation, a physical pre-separation scheme is under development. This relies upon the use of preparative gas chromatography and high pressure liquid chromatography to achieve a physical separation of complex mixtures into smaller groups of compounds, or even into single compounds. The compounds may then be effectively separated and identified on the GC/mass spectrometer system. The GC preparative system employs a modified Perkin Elmer F-11 gas chromatograph. The oven has been modified to allow the effluent vapors, after passage over the thermal conductivity detector, to pass into a glass capillary tube (1/16" wide x 8" long) held in a stainless steel outer tube. The outer tube passes first through an aluminum block maintained at the same temperature as the GC oven, and then through another aluminum block extending into a cooling bath. The exit part of the GC is fitted with a septum, which allows rapid interchange of glass capillary tubes. As each peak is detected on the GC,

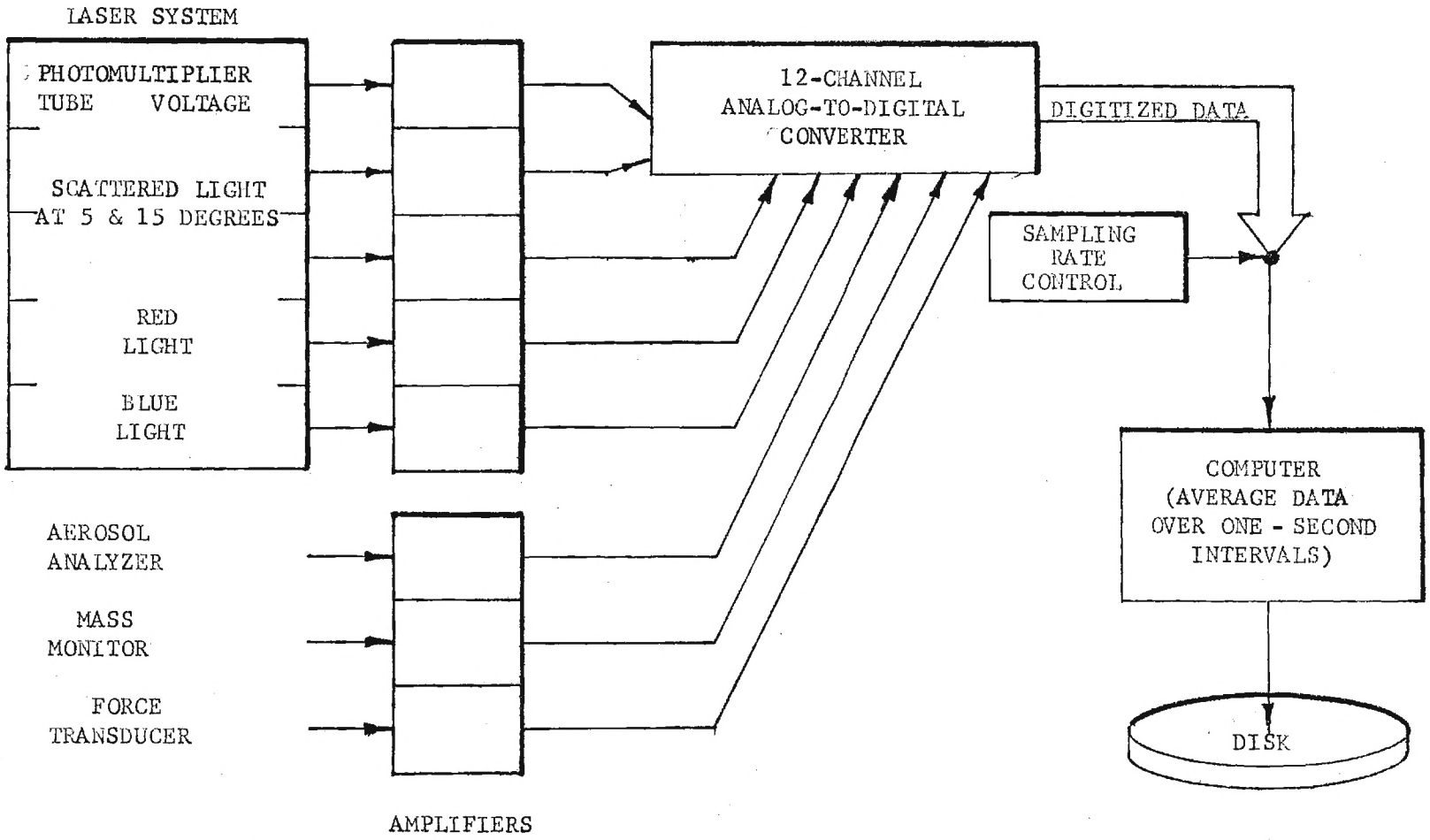

Figure 8. Data Acquisition System.

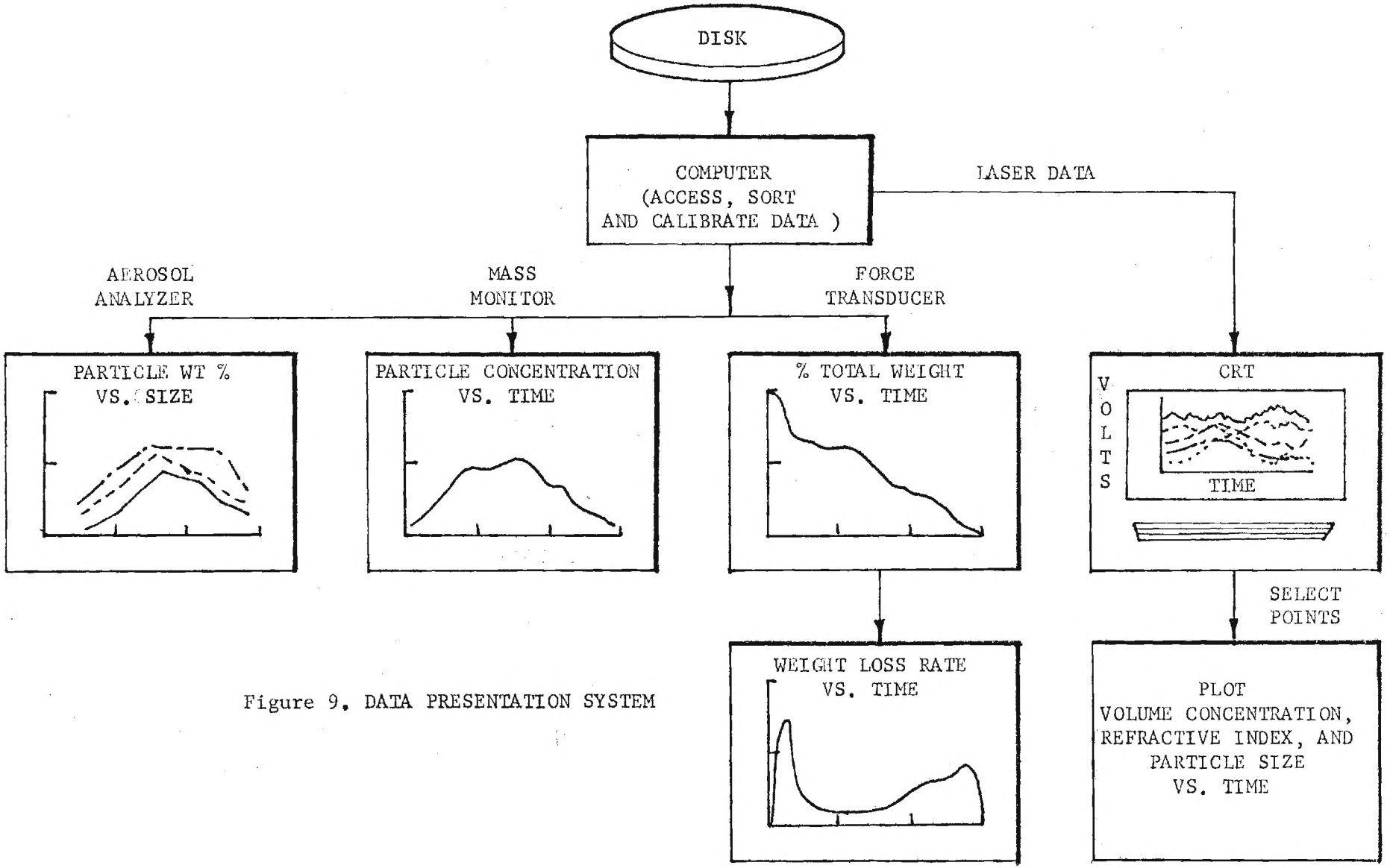

Figure 9. DATA PRESENTATION SYSTEM

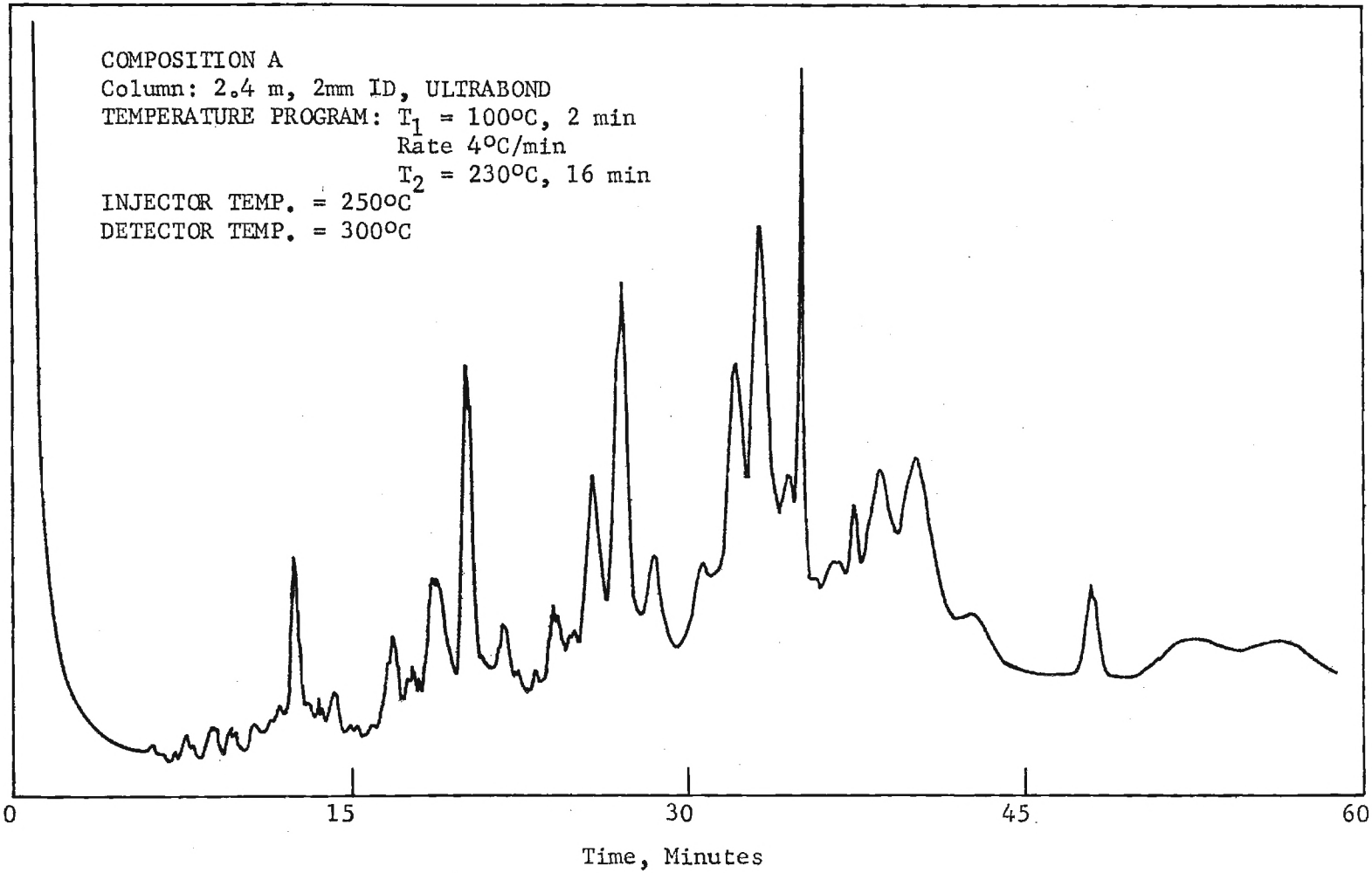

Figure 10. Typical Gas Chromatogram of Particulate Matter Collected from Smoke Produced by Smoldering Polyurethane.

the corresponding effluent is collected in the tube, which is then rapidly removed and the ends sealed for later analysis. A new tube is inserted in a few seconds in readiness for the next peak. In this manner, μg quantities of material are collected.

The collected fractions are now worked into a Readi-Vial and injected into GC columns of different polarity from that used in the preparative stage. By this means, it is hoped that complete separations of compounds can be provided and hence allow positive identification by mass spectrometry. The compounds of higher molecular weight, which are not so well suited for GC separation, are to be pre-separated by using the liquid chromatography system, prior to mass spectrometric identification.

E 10-681

PRODUCTS RESEARCH COMMITTEE

RESEARCH PROJECT NUMBER [RP-75-1-15 Revised]

INVESTIGATION OF THE PROPERTIES OF THE COMBUSTION PRODUCTS GENERATED BY FIRE-RETARDED POLYURETHANES

Quarterly Progress Report

for the period

January 1, 1977 to March 31, 1977

CO-Principal Investigators: Dr. B. T. Zinn, Regents' Professor

Dr. R. A. Cassanova, Research Engineer

Other Personnel: Dr. E. A. Powell, Assistant Professor

Dr. C. P. Bankston, Research Engineer

Dr. J. U. Rhee, Assistant Research Engineer

Dr. R. F. Browner, Assistant Professor

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia

INTRODUCTION

This quarterly report describes the efforts conducted under Products Research Committee research project number [RP-75-1-15] during the period January 1, 1977 to March 31, 1977. The grant under consideration is entitled "Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethane". The objective of this study is to determine the physical and chemical properties of the smoke particulates produced when flexible polyurethane foams are burned under different environmental conditions. The proposed tests are being conducted in a previously developed combustion products test chamber (CPTC) and the needed measurements are obtained utilizing the available sampling, optical and chemical analysis systems.

COMPOSITION OF POLYURETHANE SAMPLES

The materials tested under this program included flexible polyurethane samples of known composition which were obtained from a chemical manufacturer. The compositions of these samples were described in the first quarterly report for this grant and are repeated for reference in the Appendix. In addition, a sample was recently obtained from the National Bureau of Standards sample bank for testing in the near future. This standard sample, designated as GM23, is also being utilized by Dr. Alarie of the University of Pittsburgh in his toxicological studies. Hopefully, some useful correlations will be developed in the future when the results of these investigations are compared.

POLYURETHANE SMOKE PRODUCTION UNDER HIGH TEMPERATURE ENVIRONMENTAL CONDITIONS

The series of tests conducted during the last quarter was primarily concerned with the evaluation of the physical characteristics of the smoke produced during the combustion of flexible polyurethane foams in high temperature environmental conditions. The tests under consideration were conducted in the CPTC. The in situ optical system and a force transducer were used to measure the time variation of the smoke average particle size, the smoke optical density and the sample weight loss. The present series of tests was limited to using the above-mentioned measurement systems as the available aerosol sampling instruments cannot operate at elevated temperatures.

Weight Loss Data

Figure 1 summarizes the weight loss data which was obtained during tests at elevated temperatures with all five polyurethane samples. Since there were no significant weight loss differences between the five samples which were tested at the 100°C atmosphere the measured data for all five samples are presented in the shown band. Similarly, the weight loss data for the same five samples measured in 25°C atmospheres, which was initially described in the first quarterly report dated December 31, 1976, are also presented as a single band. A comparison of the 100°C data with the 25°C data indicates that the effect of increasing the environmental temperature is to increase the rate at which the sample is pyrolyzed and loses weight.

Average Smoke Particle Size

Figures 2 through 6 describe the time dependence of the smoke particle size measured with the five tested samples at 100°C and that of sample A at 200°C. In general, the data obtained for all five samples at 100°C indicates

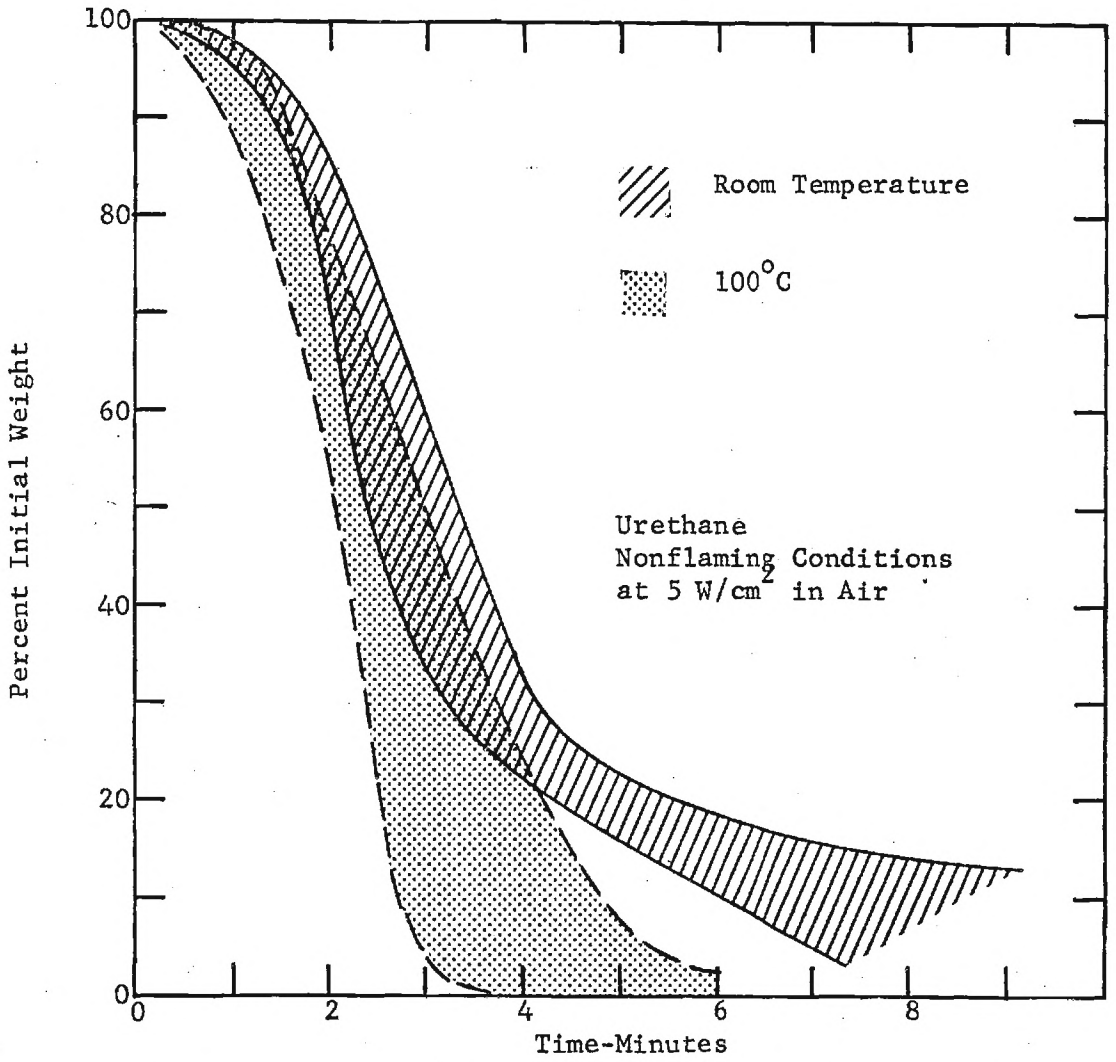

Figure 1. Comparison of Urethane Sample Weight Loss Behavior at 100°C. and Room Temperature

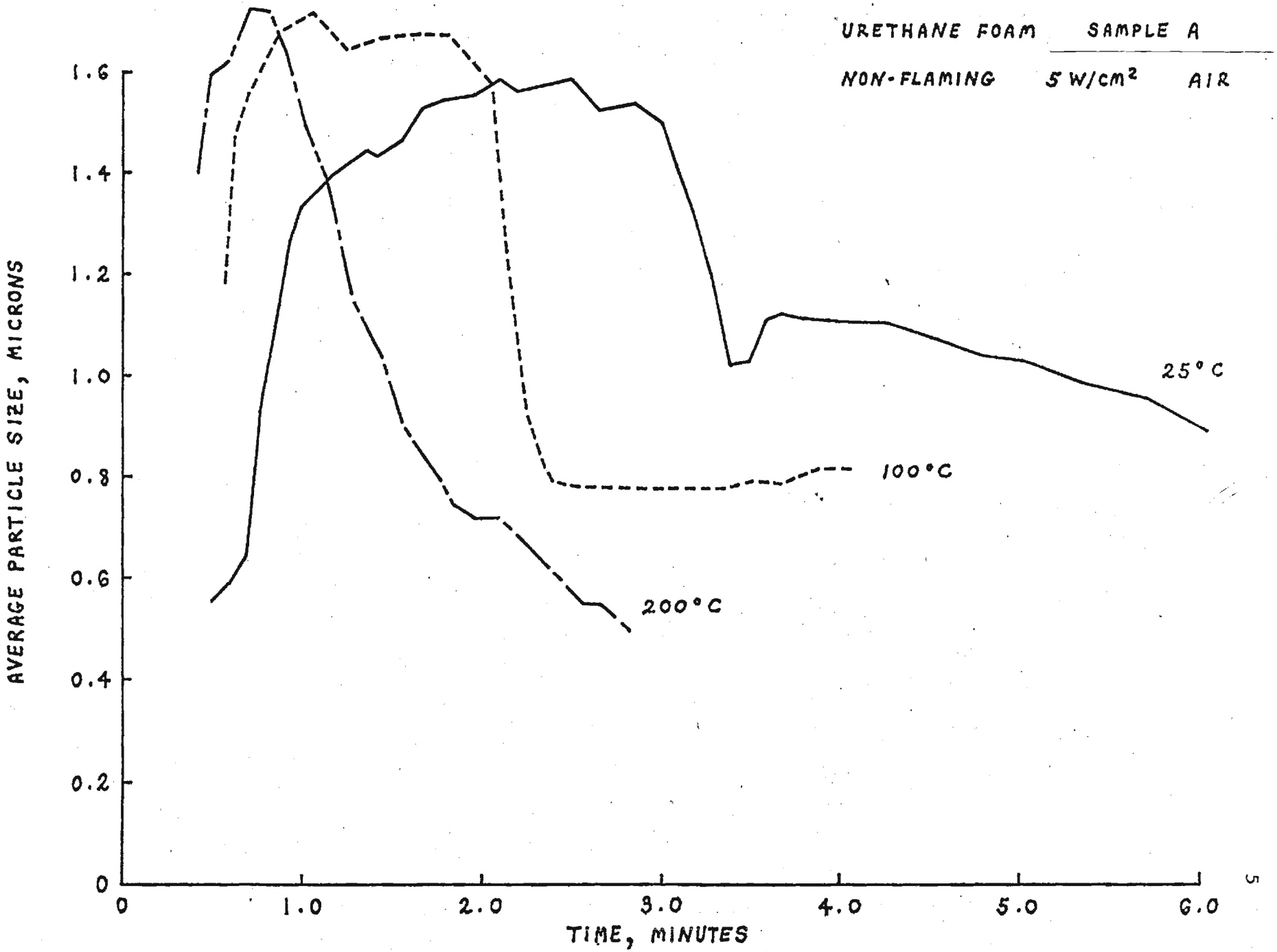

Figure 2. Effect of Temperature on the Average Smoke Particle Size Produced by Sample A.

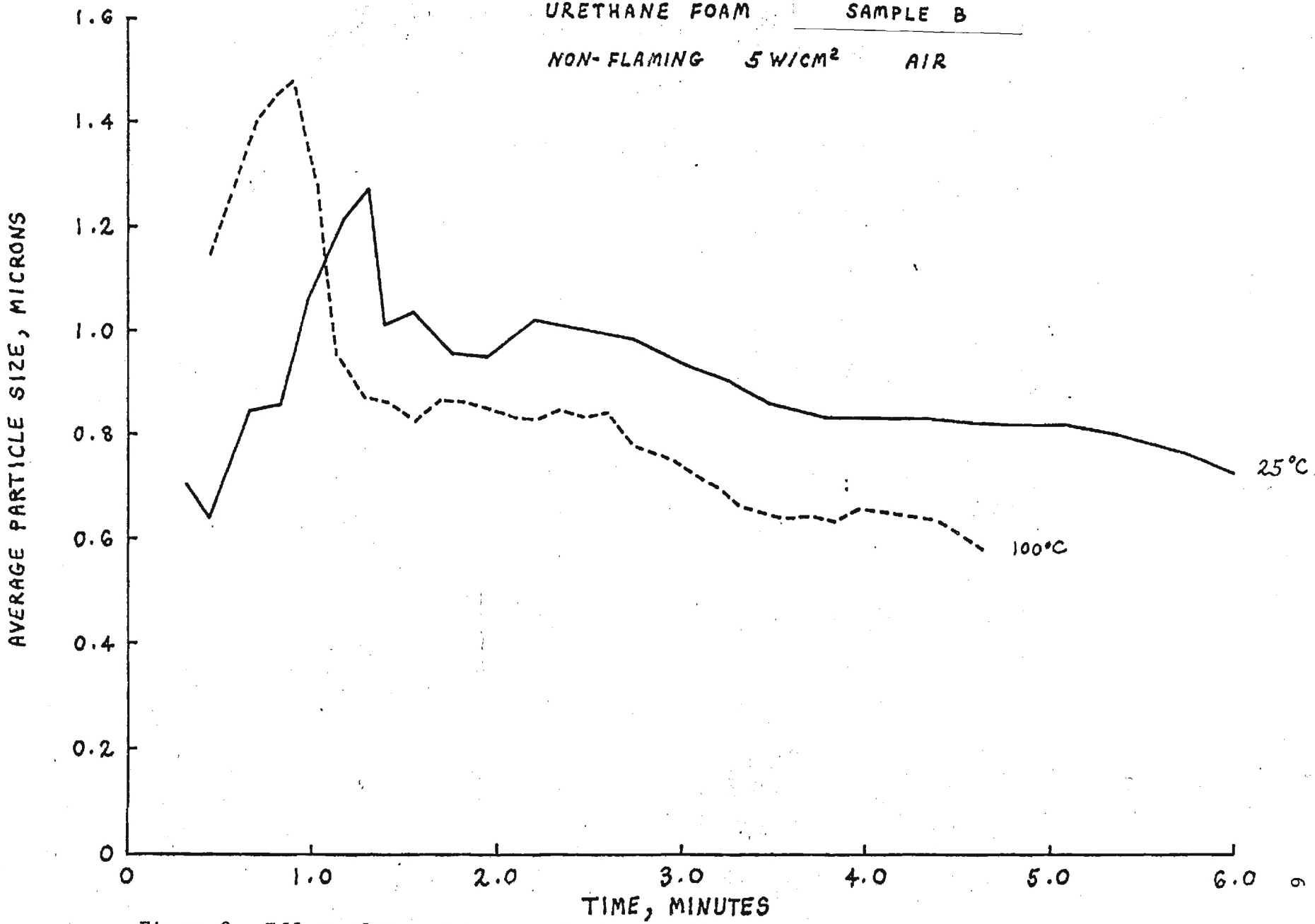

Figure 3. Effect of Temperature on the Average Smoke Particle Size Produced by Sample B.

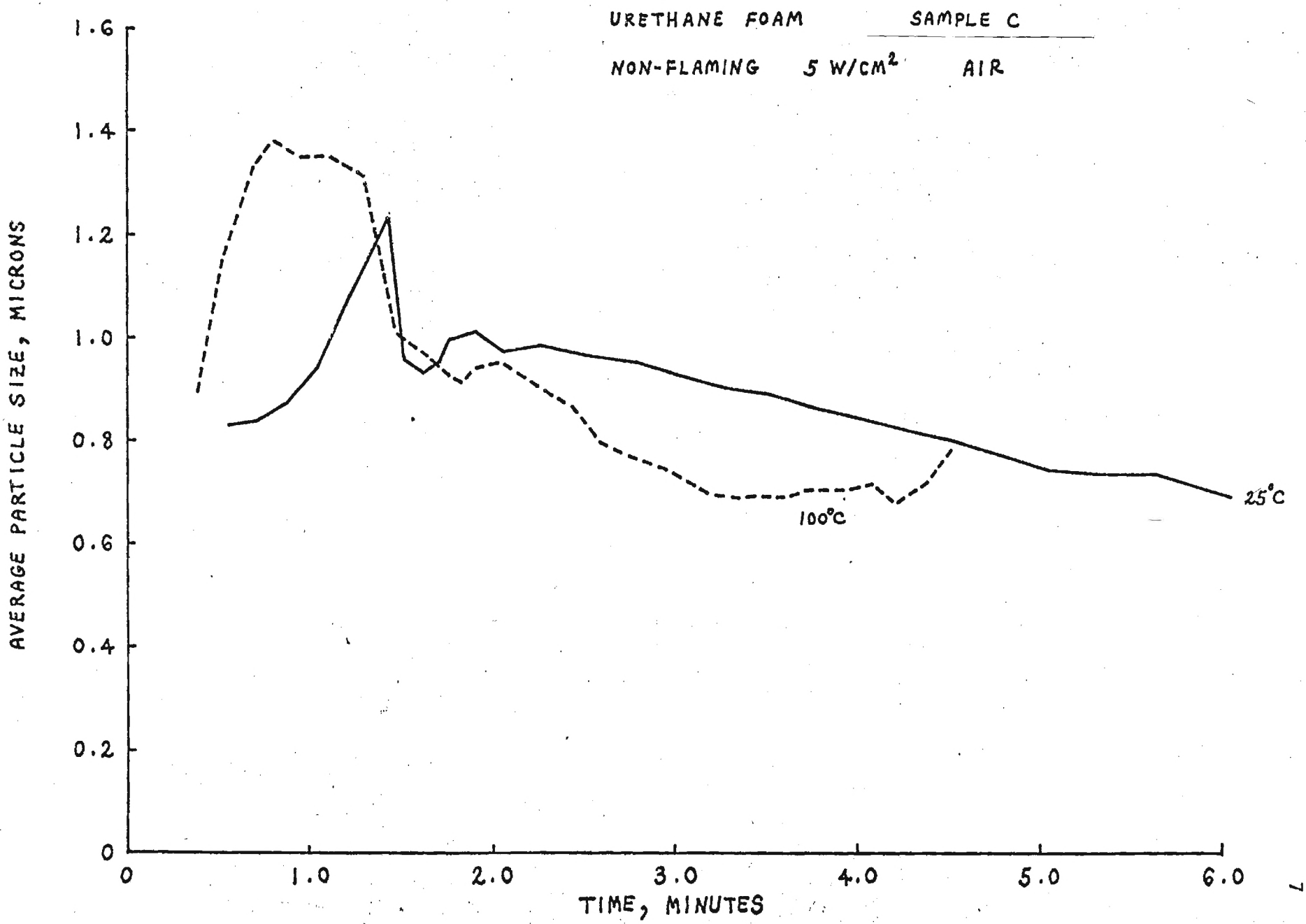

Figure 4. Effect of Temperature on the Average Smoke Particle Size Produced by Sample C.

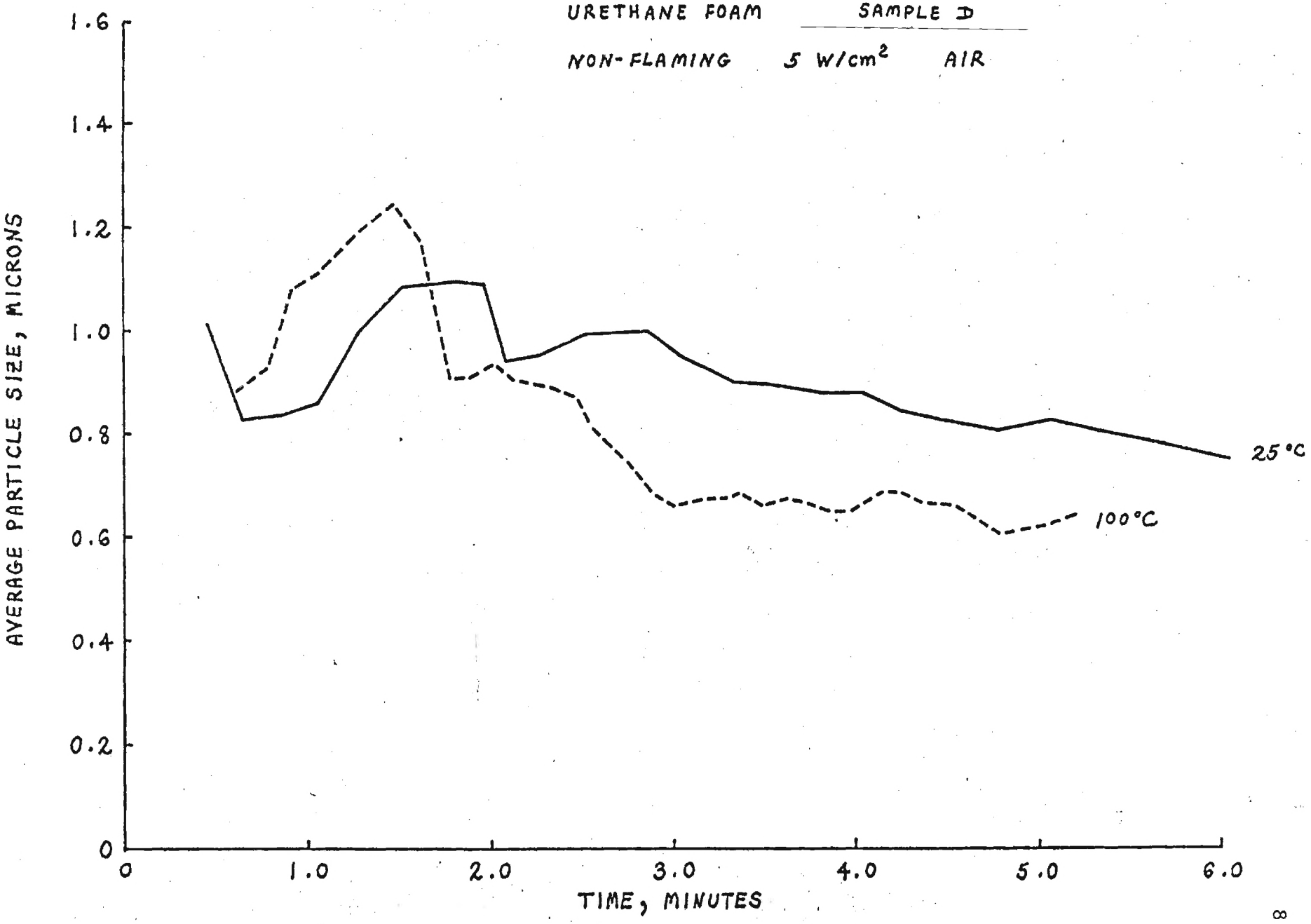

Figure 5. Effect of Temperature on the Average Smoke Particle Size Produced by Sample D.

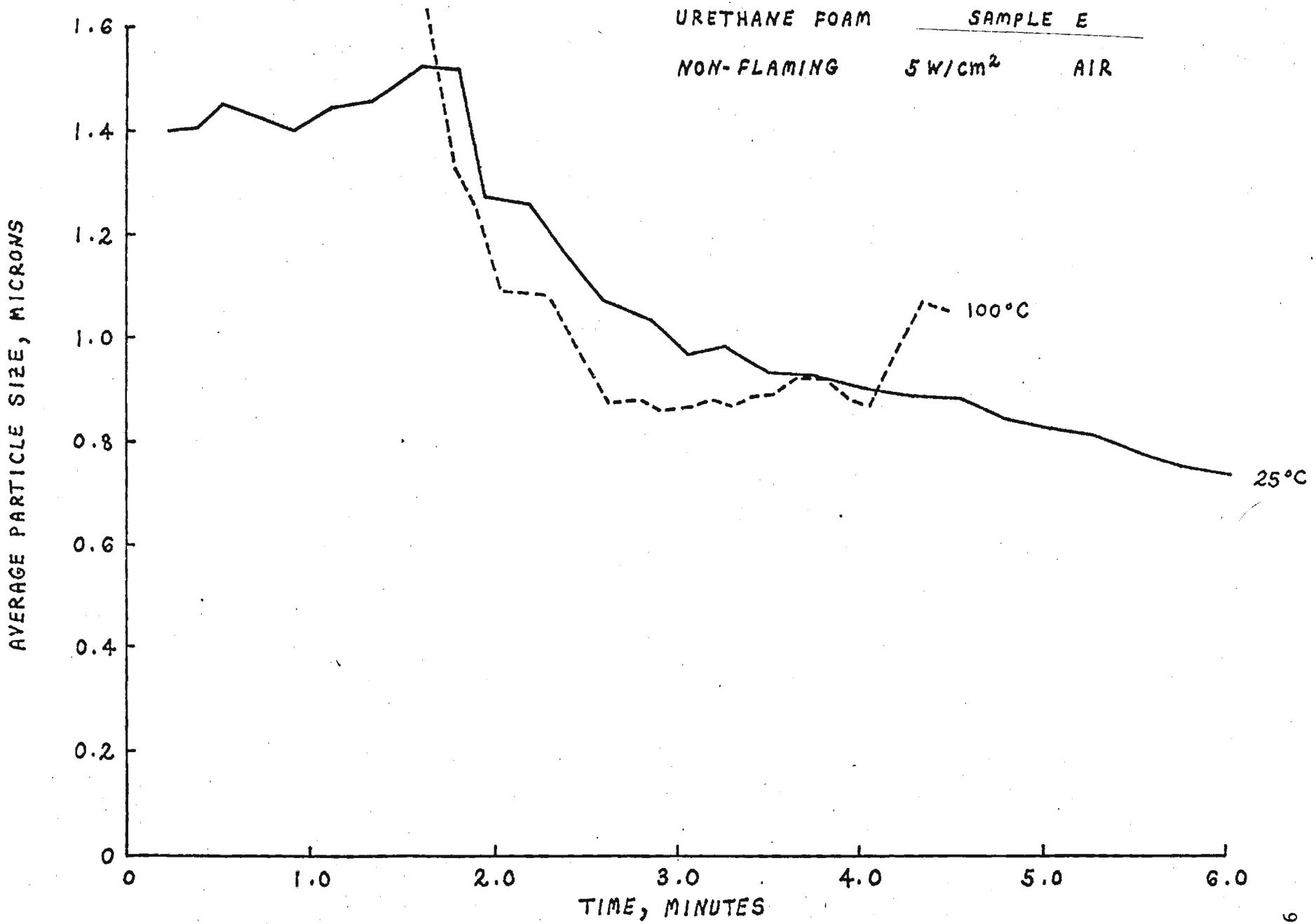

Figure 6. Effect of Temperature on the Average Smoke Particle Size Produced by Sample E.

that production of large particles in the size range of 1.2 to 1.5 microns occurs earlier in the test as the environmental temperature is increased. These results also show that after the maximum particle size is reached, somewhat smaller particles are produced by the samples of 100°C than are produced by the same sample at 25°C. The 200°C data shown in Figure 2, which was measured using sample A, gives further evidence that increasing the ventilation gas temperature causes the maximum particle size to occur earlier in the test.

Smoke Optical Density

The measurement of the smoke optical density is, by itself, an important indication of the possible reduction in visibility caused by the smoldering of polyurethanes. In addition, the optical density, together with the particle size measurements, provides a measure of the variation of particulate concentration.

Figures 7 through 11 show the optical densities produced by the five samples, under smoldering conditions, when they are exposed to a 5 W/cm^2 heat flux. Examination of these figures show that, in general, increasing the environmental temperature resulted in a reduction in the maximum optical density or maximum light obscuration due to smoke production. This data show that for samples A, B and E that the maximum optical density is reached earlier in the test under high temperature conditions. The results for sample A, shown in Figure 7, indicate that increasing the temperature to 200°C causes the optical density to be significantly reduced below the levels measured at 25°C and 100°C. It should be noted that the optical density is lowest in the beginning of each test when the average particle size is the largest. These combined trends imply that the particulate concentration is very low at this point in the test. Since concentration is low, the

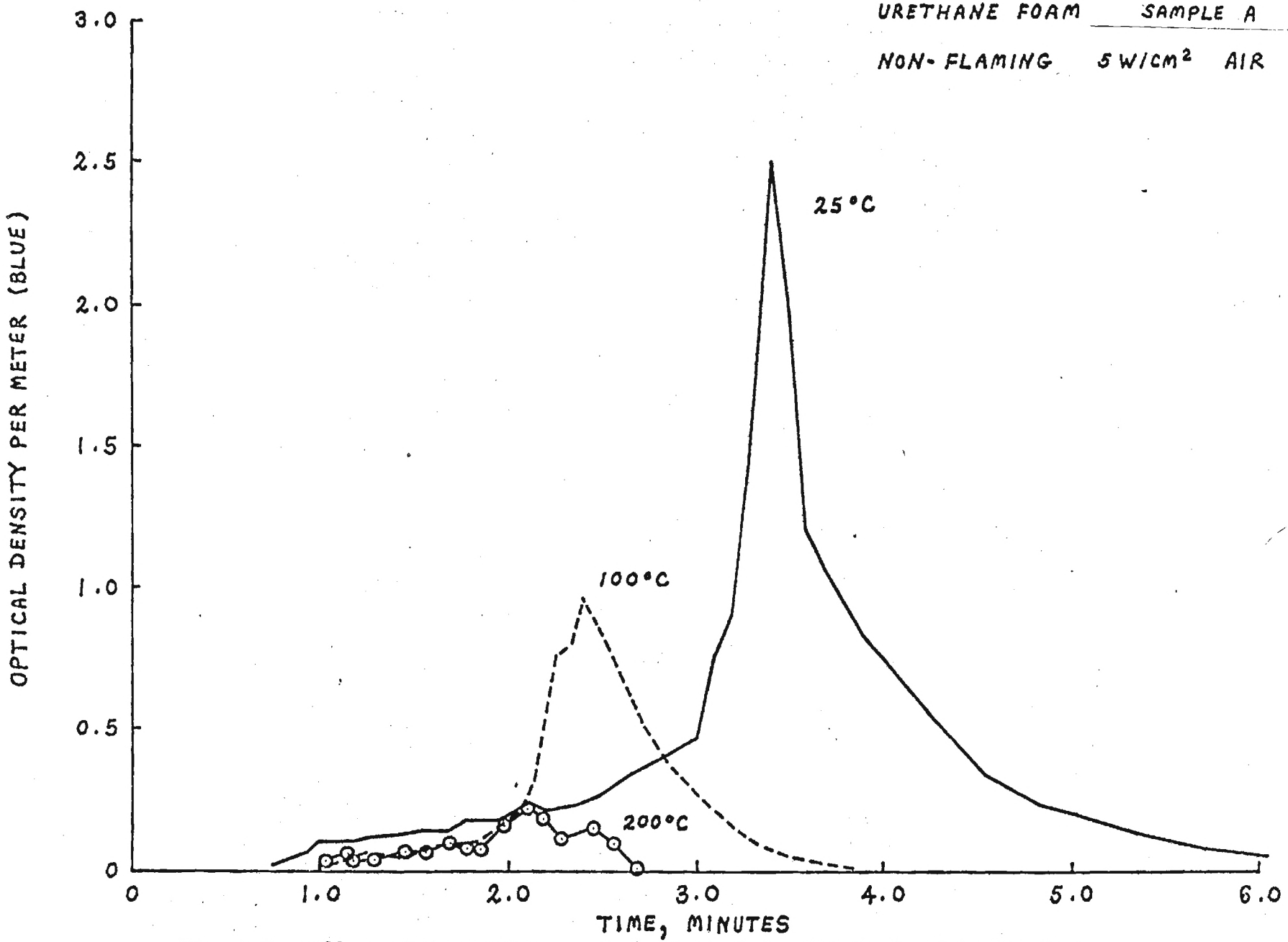

Figure 7. Effect of Temperature on Smoke Optical Density Produced by Sample A.

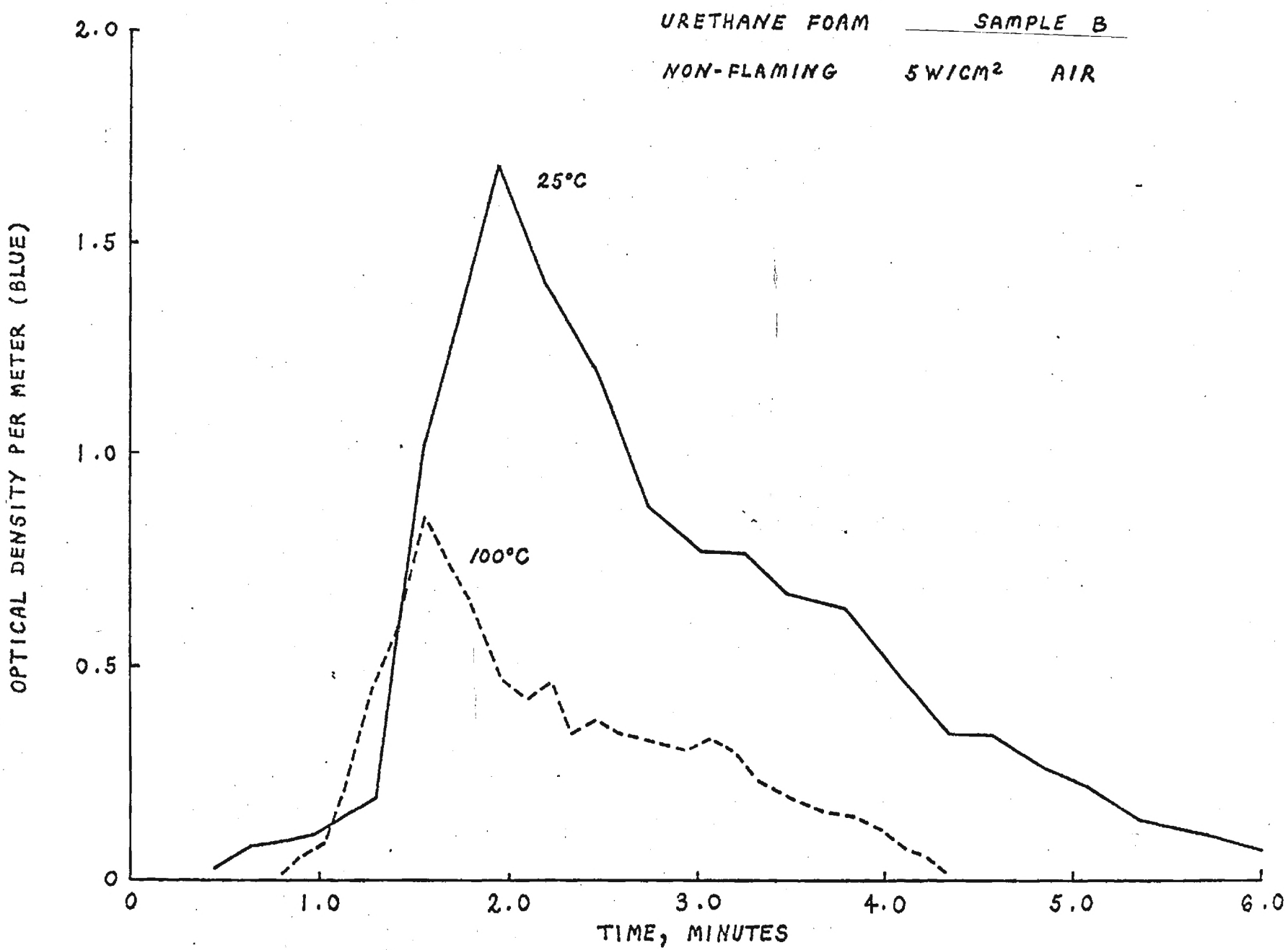

Figure 8. Effect of Temperature on Smoke Optical Density Produced by Sample B.

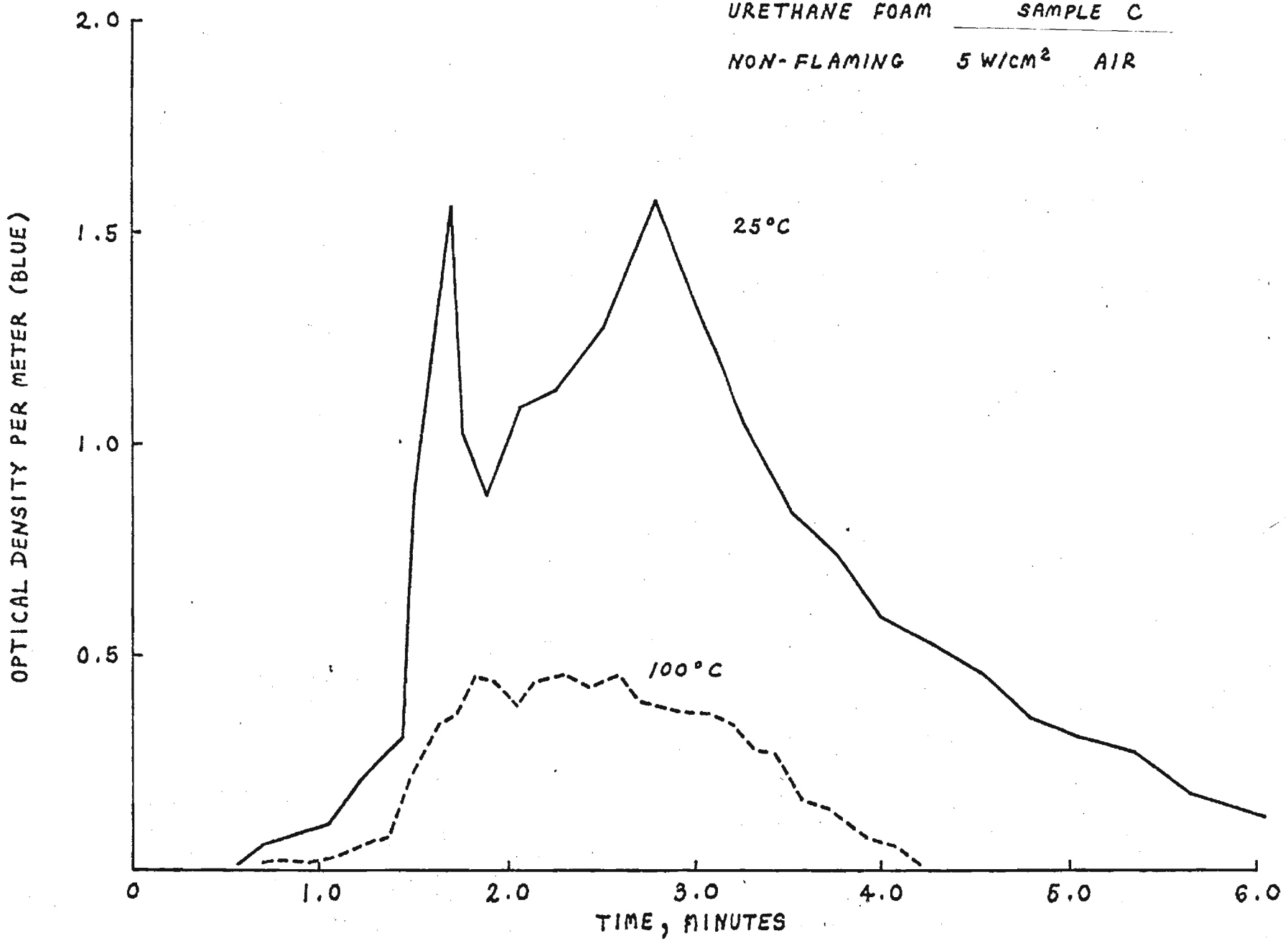

Figure 9. Effect of Temperature on Smoke Optical Density Produced by Sample C.

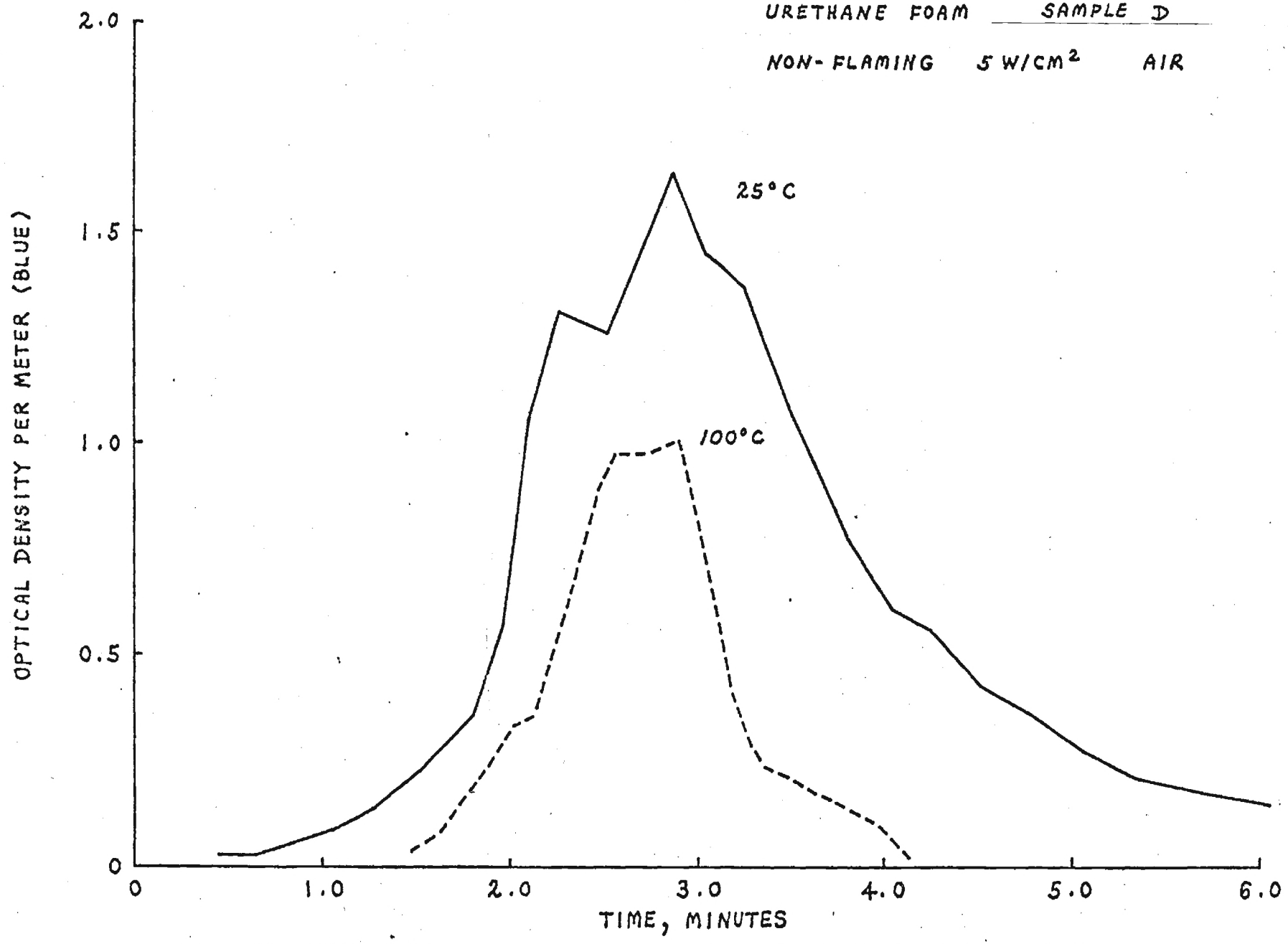

Figure 10. Effect of Temperature on Smoke Optical Density Produced by Sample D.

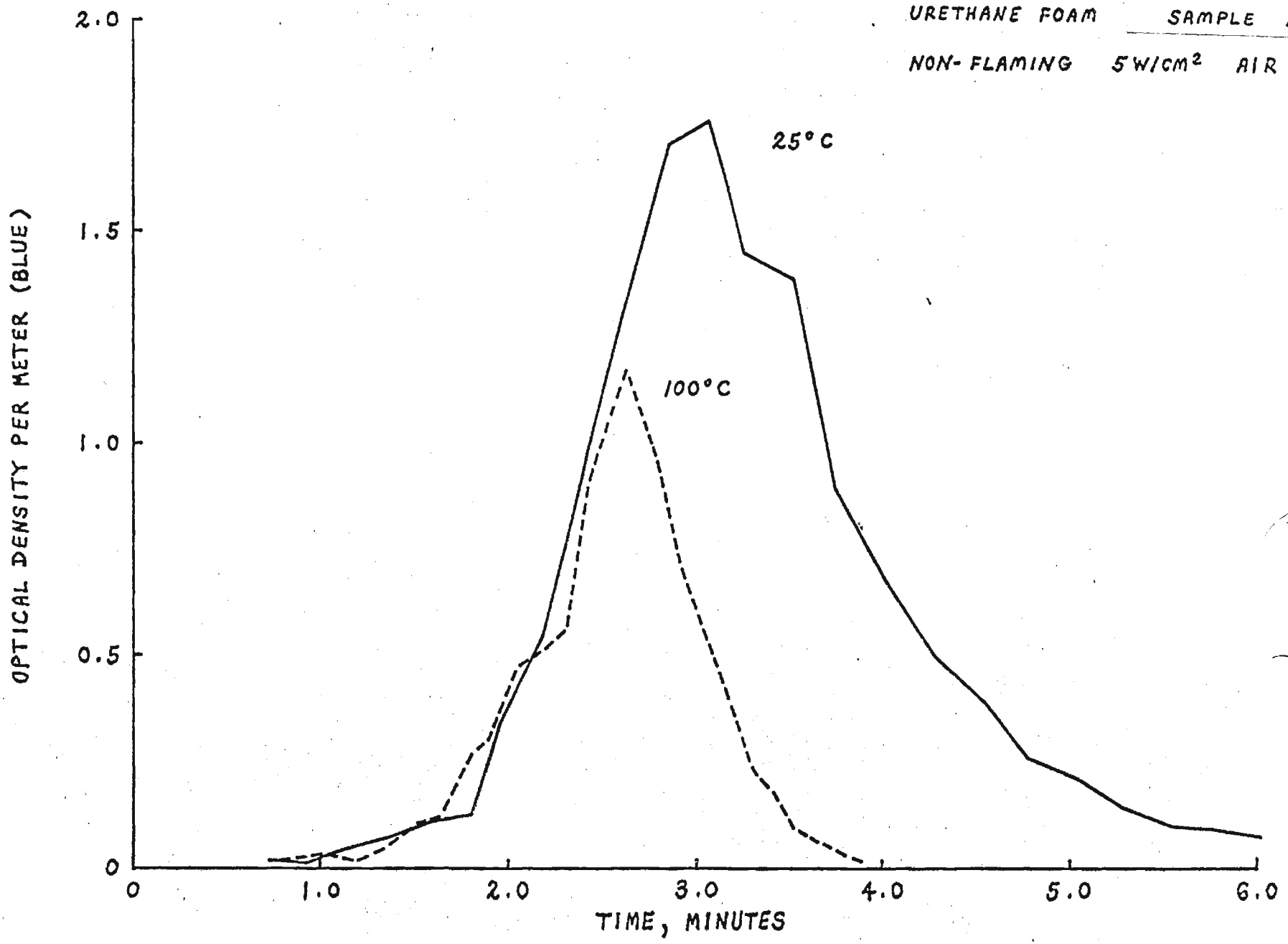

Figure 11. Effect of Temperature on Smoke Optical Density Produced by Sample E.

effects of coagulation on the particle size would be minimal during this portion of the test. Therefore, the occurrence of large particles is most likely caused by formation phenomena occurring at or near the sample face.

Summary

Tests conducted to date indicate that an increase in the temperature of the environment is associated with an increase in the pyrolysis (or weight loss) rate of the sample. However, the higher temperature also reduces the amount of pyrolysate which actually condenses to form the liquid and solid particulate matter.

CHEMICAL ANALYSIS OF PARTICULATES

The development of a chemical analysis scheme for the separation of the compounds contained in the particulates continued during this quarter. The micro-preparative gas chromatography system which was described in the last report has been constructed, and a program of preparative GC work is underway. The primary intention of this program is to "clean-up" the very complex mixture of organic compounds which are collected on the sample filters and to allow more effective mass spectrometric identification of the individual chemical groups.

The development of the methodology for using the high pressure liquid chromatograph (HPLC) to preseparate the complex samples before injection into the gas chromatograph/mass spectrometer system was continued. Samples of the particulate matter which were extracted with methylene chloride were injected into the HPLC in order to make a preliminary analysis of sample components by comparison with the retention times of known, standard compounds.

During the next quarter, the chemical analysis effort will initially concentrate on identifying the more volatile, low molecular weight compounds which are well suited for preparative GC work. By choosing column packing materials of different polarity for the preparative GC and for the analytical GC prior to injection into the mass spectrometer, it should be possible to achieve greatly improved resolution of the more volatile compounds.

APPENDIX

POLYURETHANE SAMPLE COMPOSITIONS

FLEXIBLE POLYURETHANE FOAM

FORMULATIONS - PARTS BY WEIGHT

COMPOSITION	A	B	C	D	E
Poly-G® 3030 PG	100.0	100.0	100.0	100.0	100.0
TDI 80	51.3	51.3	51.3	51.3	51.3
Water	4.0	4.0	4.0	4.0	4.0
Thermolin® 101	-	8.0	-	-	-
HB-32	-	-	8.0	-	-
FR-2	-	-	-	-	8.0
2XC20	-	-	-	8.0	-
L-5710	1.0	1.0	1.0	1.0	1.0
-C-2	0.250	0.250	0.250	0.225	0.225
Dabco 33 LV	0.300	0.300	0.300	0.300	0.300

CHEMICALS

Olin Poly-G® 3030 PG	is Glycerin propoxylated to a molecular weight of about 3000.
Olin TDI-80	is a mixture of 80% 2,4 and 20% 2,6 toluene diisocyanate.
Union Carbide L-5710	is a dimethyl siloxane polymer with Si-C-O linkages - also contains ethylene oxide-propylene oxide co-polyethers.
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COMMERCIAL NON-REACTIVE

FLAME RETARDANTS

Manufacturer & Name	Chemical Compound	% Analysis P	Cl	Br
Monsanto 2XC20	Chlorinated Diphosphate Ester	10.6	35.2	-
Stauffer FR 2	Tris(2,3 Dichloro Propyl) Phosphate	7.2	49.1	-
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Olin Thermolin^{R} 101	Tetrakis (2-chloro ethyl) ethylene diphosphate	13.0	31.0	-

PRODUCTS RESEARCH COMMITTEE

RESEARCH PROJECT NUMBER [RP-75-1-15 Revised]

INVESTIGATION OF THE PROPERTIES OF THE COMBUSTION PRODUCTS GENERATED BY FIRE-RETARDED POLYURETHANES

Quarterly Progress Report

for the period

April 1, 1977 to June 30, 1977

Co-Principal Investigators: Dr. B. T. Zinn, Regents' Professor

Dr. R. A. Cassanova, Sr. Research Engineer

Other Personnel: Dr. E. A. Powell, Assistant Professor

Dr. C. P. Bankston, Research Engineer

Dr. J. U. Rhee, Assistant Research Engineer

Dr. R. F. Browner, Assistant Professor

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia

INTRODUCTION

This quarterly report describes the efforts conducted under Products Research Committee research project number [RP-75-1-15] during the period April 1, 1977 to June 30, 1977. The grant under consideration is entitled "Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethane". The objective of this study is to determine the physical and chemical properties of the smoke particulates produced when flexible polyurethane foams are burned under different environmental conditions. Tests have been conducted in a previously developed combustion products test chamber (CPTC) and the needed measurements have been obtained utilizing the available sampling, optical and chemical analysis systems. The materials tested under this program include flexible polyurethane samples of known composition which were obtained from a chemical manufacturer. The compositions of these samples were described in the first quarterly report for this grant and are repeated for reference in the Appendix.

POLYURETHANE SMOKE PRODUCTION UNDER SMOLDERING, LOW TEMPERATURE ENVIRONMENTAL CONDITIONS

Tests of the five flexible urethane samples under nonflaming conditions in a room temperature (25°C) ventilation gas (air) have been completed. During the 3rd quarter, measurements were obtained of the characteristics of the smoke produced under nonflaming conditions at 10 W/cm^2 radiant flux. The results of these tests are presented in Figures 1 through 7. Also, low temperature tests of the urethane samples at 2.5 W/cm^2 radiant flux were initiated. However, it was found that for the test conditions established in the CPTC (vertical sample mounting and continuous ventilation), the heating rate of 2.5 W/cm^2 results in insufficient sample decomposition to produce

measurable quantities of smoke. Thus, no data at the 2.5 W/cm^2 heating rate is currently available.

Results of sample weight loss measurements at 10 W/cm^2 are given in Figure 1. Since there were no significant differences in weight loss characteristics among the samples tested at 10 W/cm^2, the data are presented in the indicated band. For comparison purposes, similar data from results obtained at 5 W/cm^2 is also plotted in this figure. These results show that the samples decompose much faster at 10 W/cm^2 when compared to the 5 W/cm^2 radiant flux, and that little measurable sample mass remains at the end of tests at the higher heating rate.

Figures 2 and 3 provide size distributions obtained utilizing the cascade impactor which collects samples over the entire test period. As observed in the results of tests at 5 W/cm^2 (see the quarterly report dated December 31, 1976), there are differences among the five samples in the total particulate weight which is generated by a given sample. In these data, Compositions C and D produced a lower concentration of larger particles than the other compositions while Compositions A and E produced the greatest total mass of particles. These data also show that Compositions C and D produced considerably less particulate mass at 10 W/cm^2 when compared to the earlier results obtained at 5 W/cm^2.

Figures 4 and 5 present time-resolved average particle size variations during tests at 10 W/cm^2 radiant heat flux. They show that Compositions C and D produce smaller particles for longer periods than the other compositions, which is consistent with the cascade impactor data. Also, the particle size peak for all samples occurs much earlier at 10 W/cm^2 radiant flux than in the 5 W/cm^2 tests. The smoke optical density behavior shown in Figures 6 and 7 is characterized by peaks at t = 1 minute for all samples;

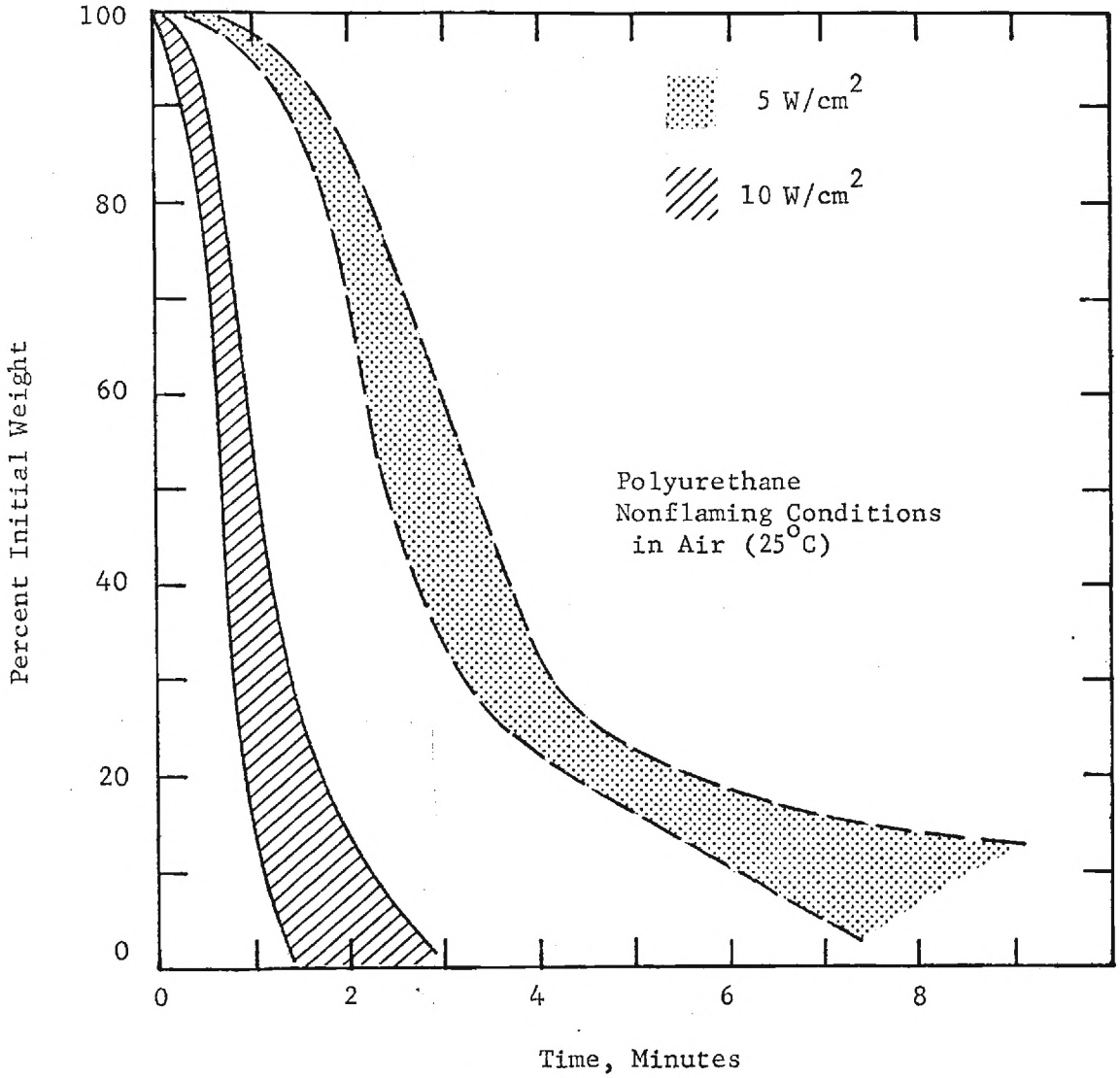

Figure 1. Comparison of Polyurethane Sample Weight Loss Behavior at 5 W/cm^2 and 10 W/cm^2 in Air (25°C)

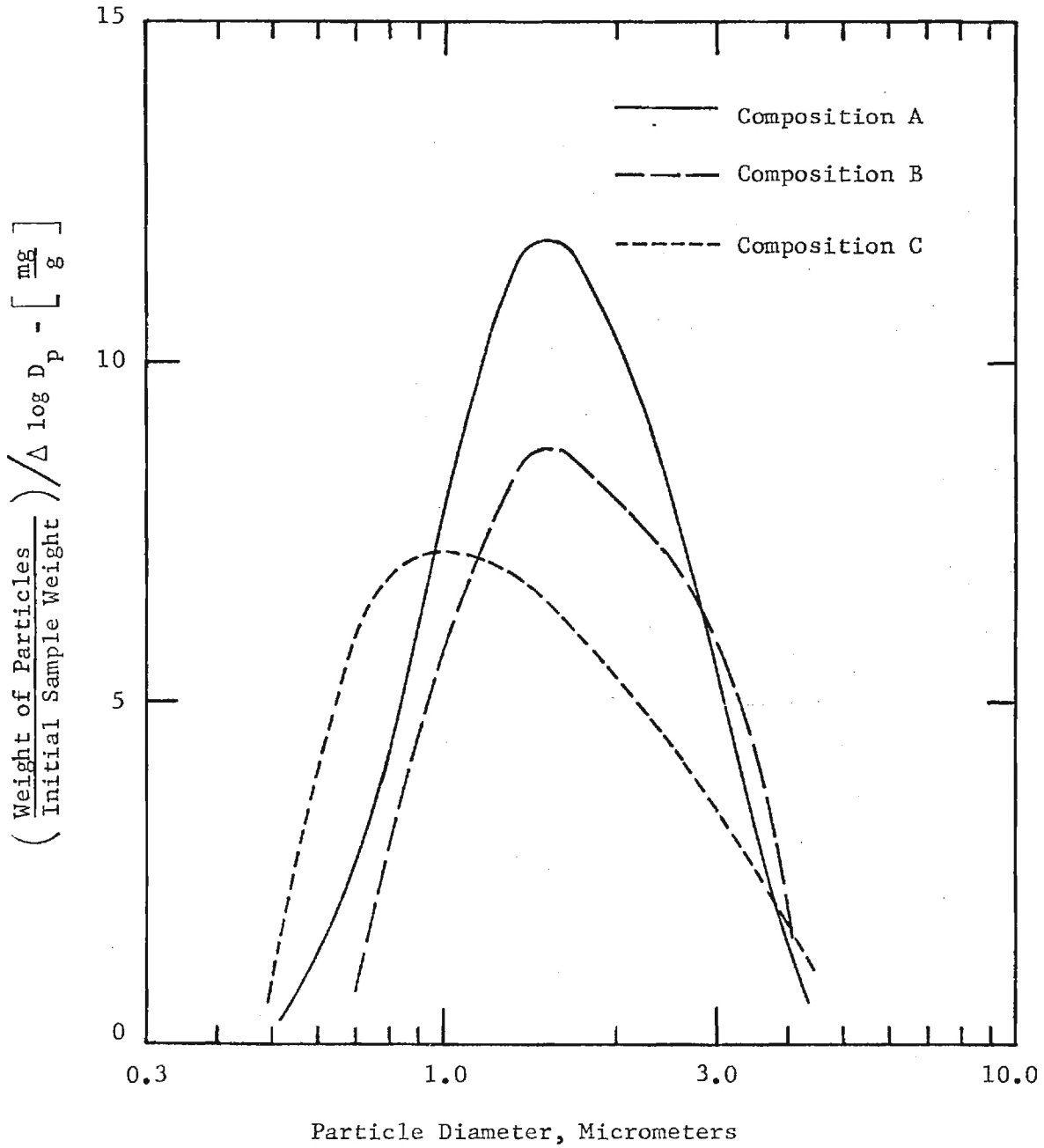

Figure 2. Integrated Smoke Particle Size Distributions for Flexible Polyurethanes - Nonflaming Conditions at 10 W/cm^2 in Air (25°C).

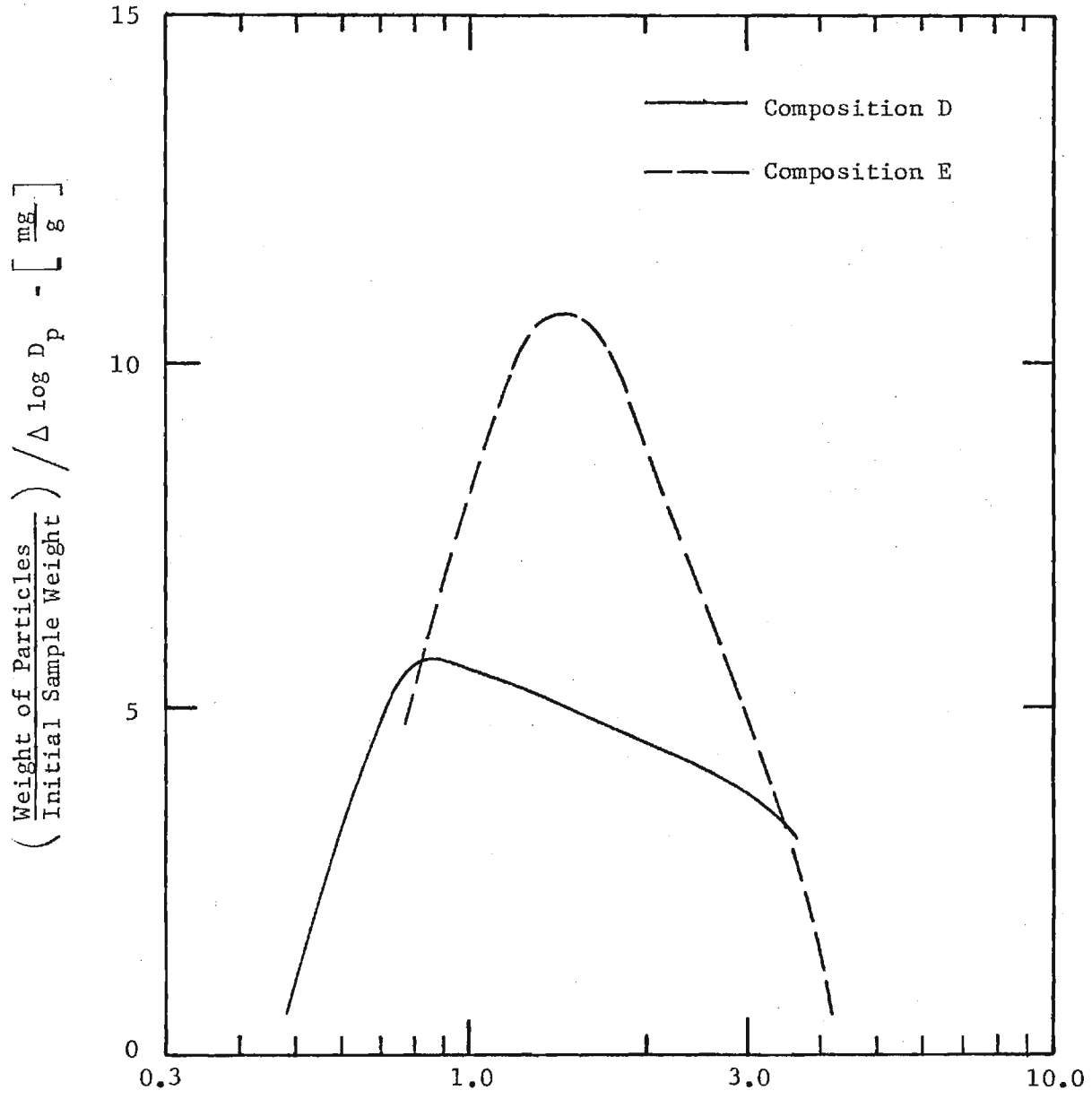

Figure 3. Integrated Smoke Particle Size Distributions for Flexible Polyurethanes - Nonflaming Conditions at 10 W/cm^2 in Air (25°C).

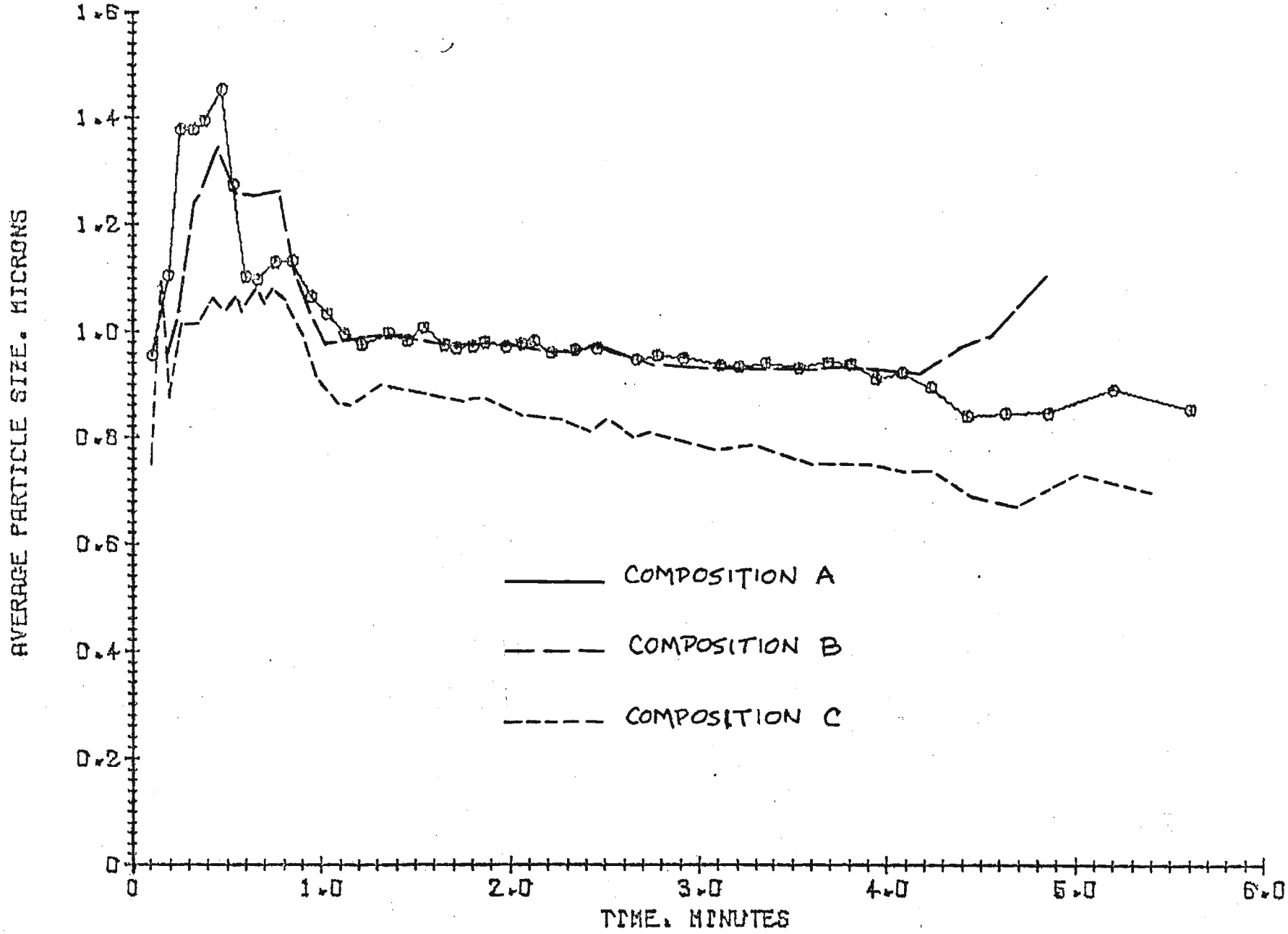

Figure 4. Time Resolved Smoke Particle Size Behavior at 10 W/cm^2 - Nonflaming Polyurethanes.

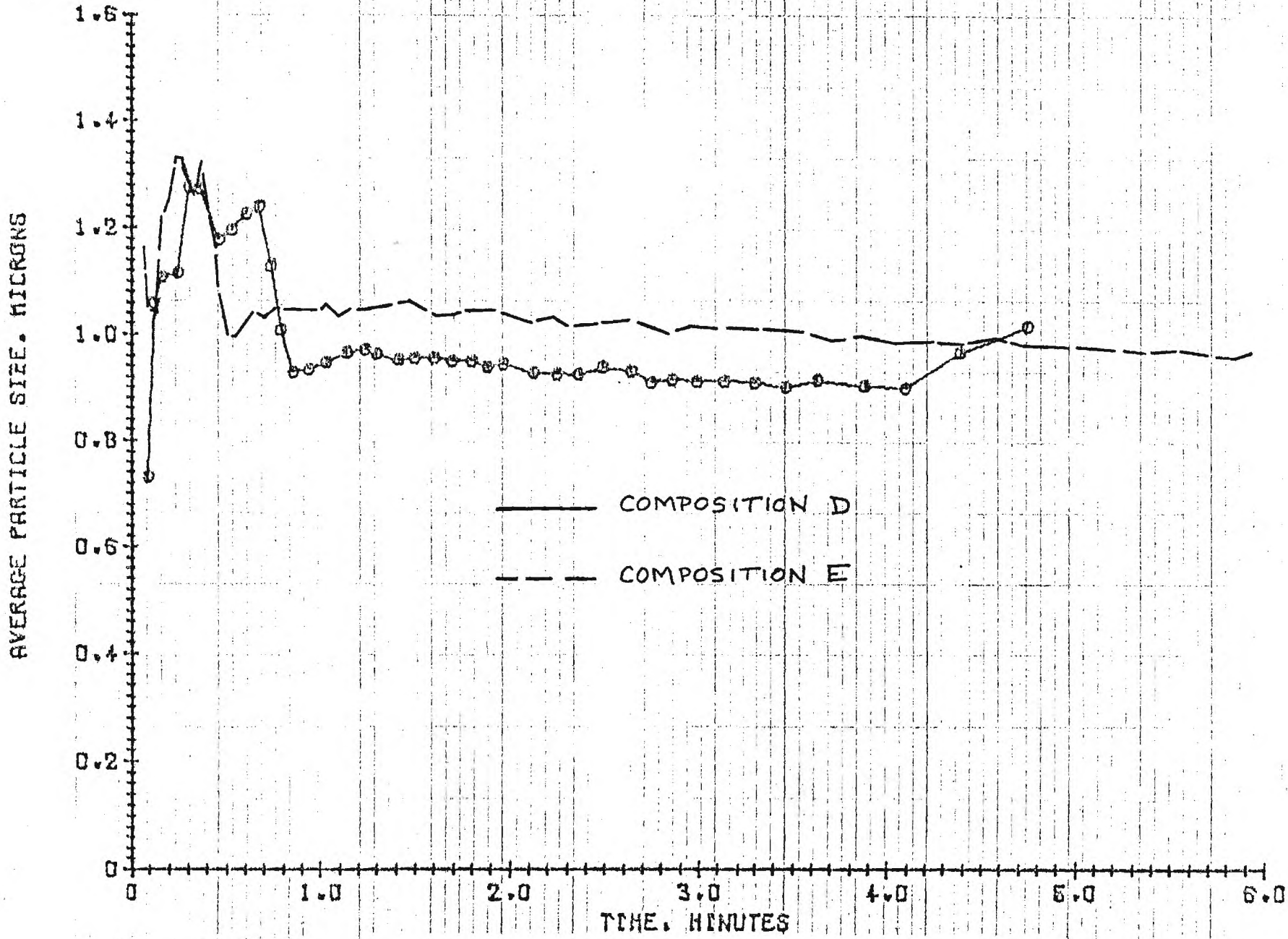

Figure 5. Time Resolved Smoke Particle Size Behavior at 10 W/cm^2 - Nonflaming Polyurethanes.

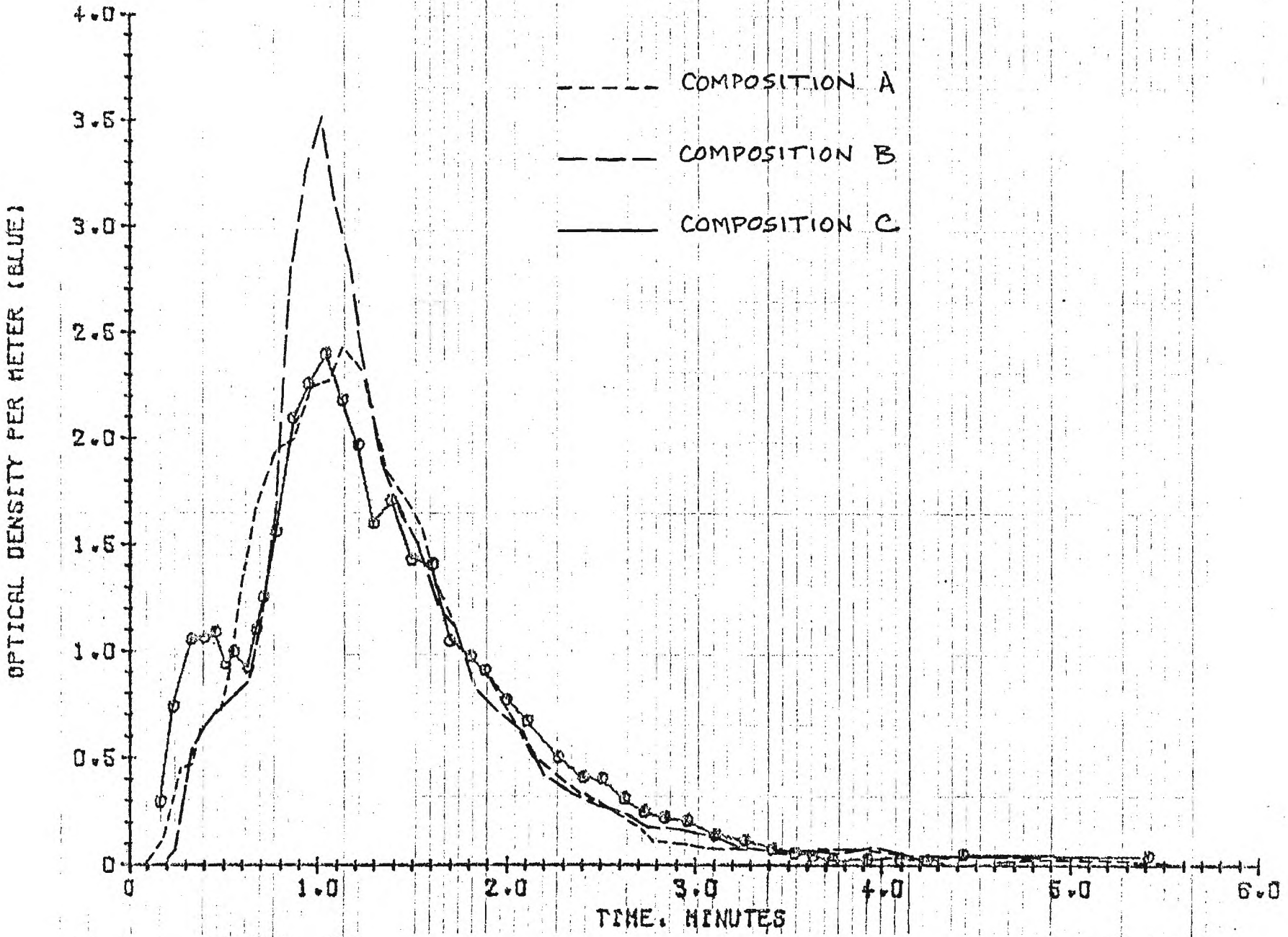

Figure 6. Smoke Optical Density Behavior at 10 W/cm^2 - Nonflaming Polyurethanes.

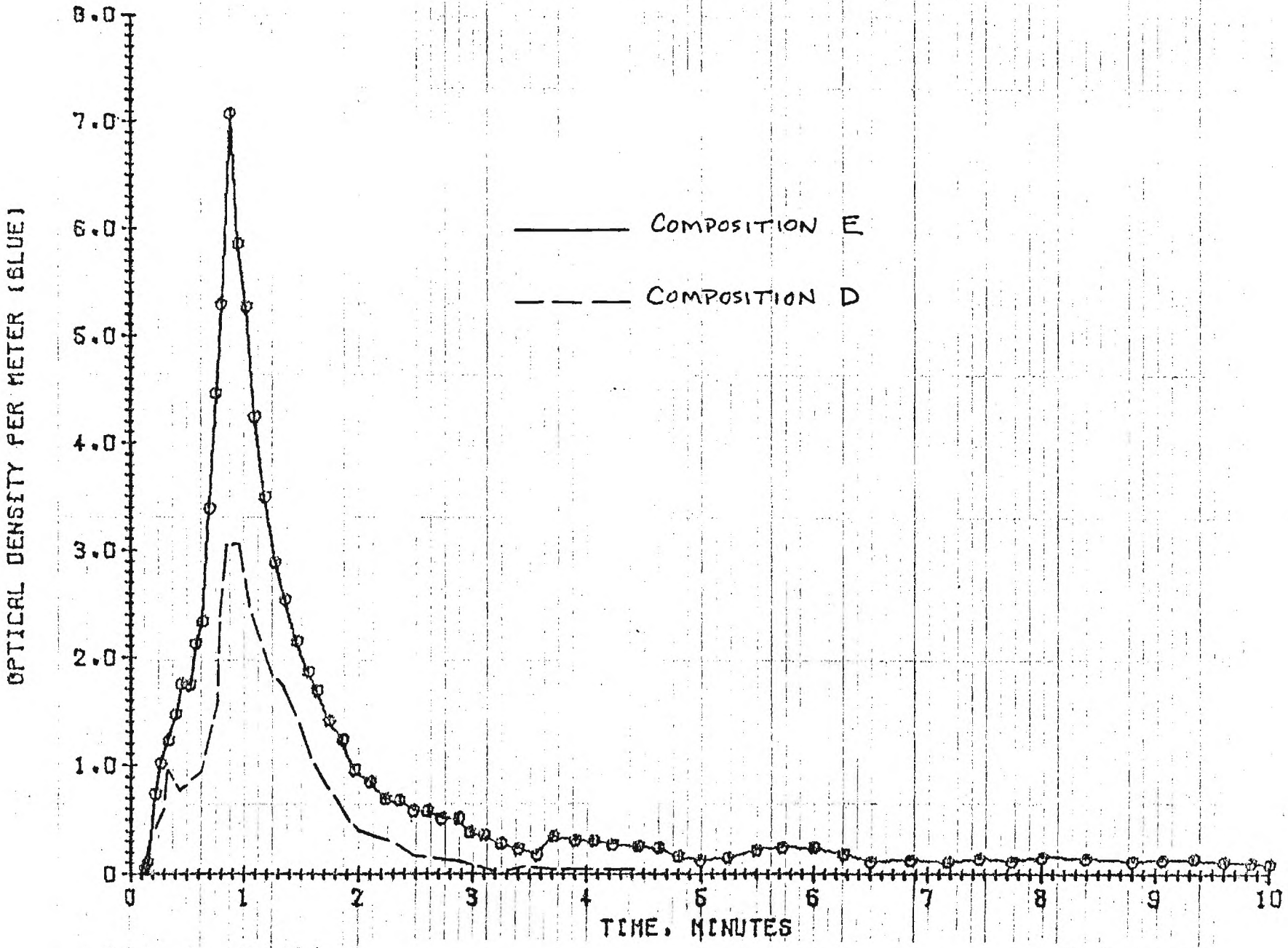

Figure 7. Smoke Optical Density Behavior at 10 W/cm^2 - Nonflaming Polyurethanes

these peaks appear earlier than the corresponding peaks observed in 5 W/cm^2 tests. The maximum optical densities in 10 W/cm^2 tests were greater for Compositions B and E.

POLYURETHANE SMOKE PRODUCTION UNDER SMOLDERING, HIGH TEMPERATURE ENVIRONMENTAL CONDITIONS

During the 3rd quarter, nonflaming, high temperature tests of the five polyurethane samples were completed. Measurements of the physical characteristics of smoke generated by smoldering samples have been taken for ventilation gas (air) temperatures of 100°C, 200°C and 300°C, while the samples were exposed to 5 W/cm^2 radiant flux. This series of tests has been limited to in situ optical system and force transducer measurements, since the aerosol sampling system instrumentation cannot be operated at elevated temperatures.

Figures 8 and 9 summarize the weight loss data which have been obtained at high temperatures with the five polyurethane samples. The data are presented in characteristic bands for each ventilation gas temperature, including room temperature (25°C) data. The results show that the effect of increasing the environmental temperature is to increase the rate at which the sample is pyrolyzed and loses weight.

Figures 10-14 describe the time dependence of the smoke particle mean diameter, D_{32}, measured for each of the urethane samples at all ventilation gas temperatures under consideration. The data indicates that for Compositions A, D and E the production of the largest particles occurs earlier in the test as the environmental temperature increases. The results for those three compositions also show that in general, after the maximum particle size is reached, somewhat smaller particles are produced for each increase in ventilation gas temperature. These trends are also observed for Compositions B and C although exceptions are noted at 200°C in the results for

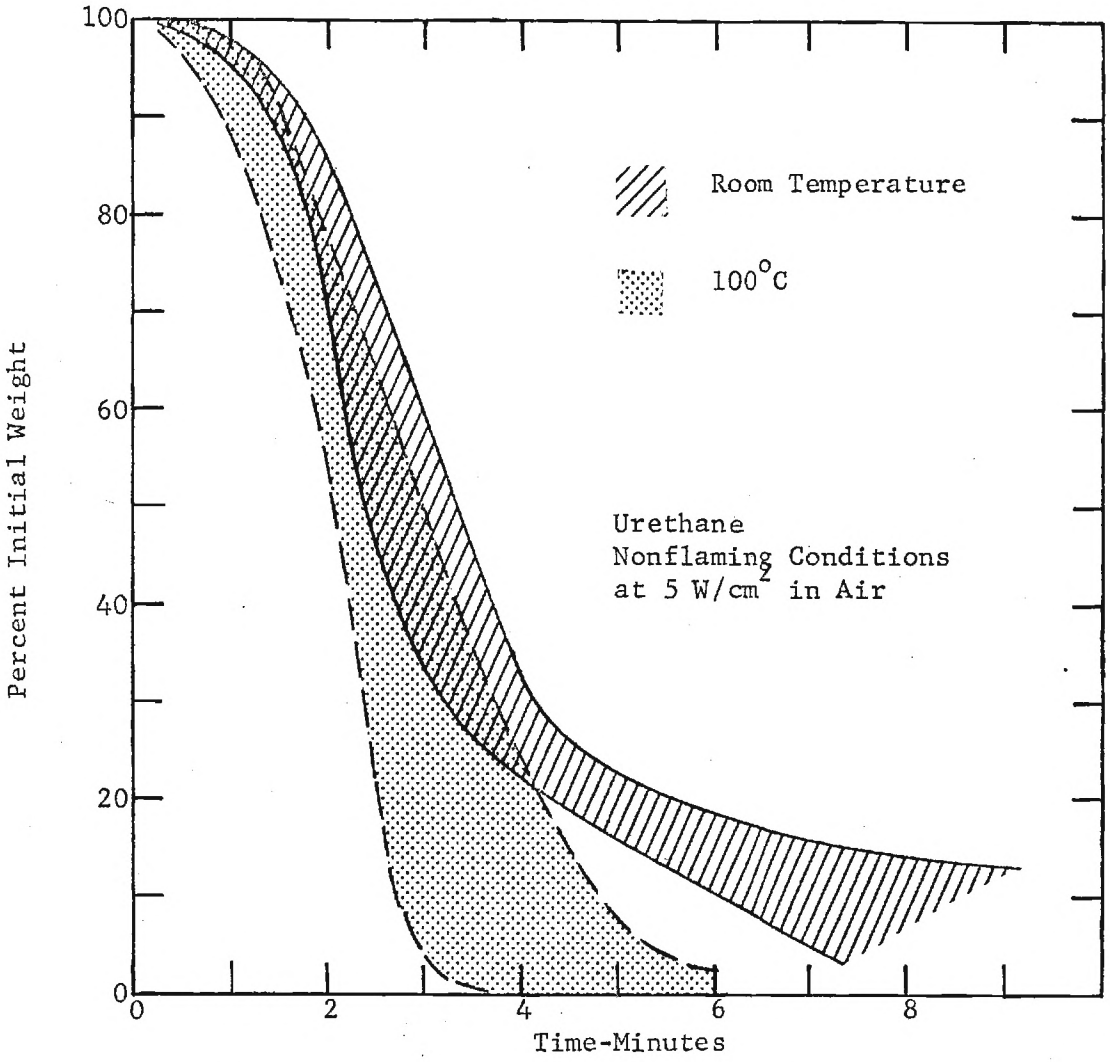

Figure 8. Comparison of Urethane Sample Weight Loss Behavior at 100°C. and Room Temperature

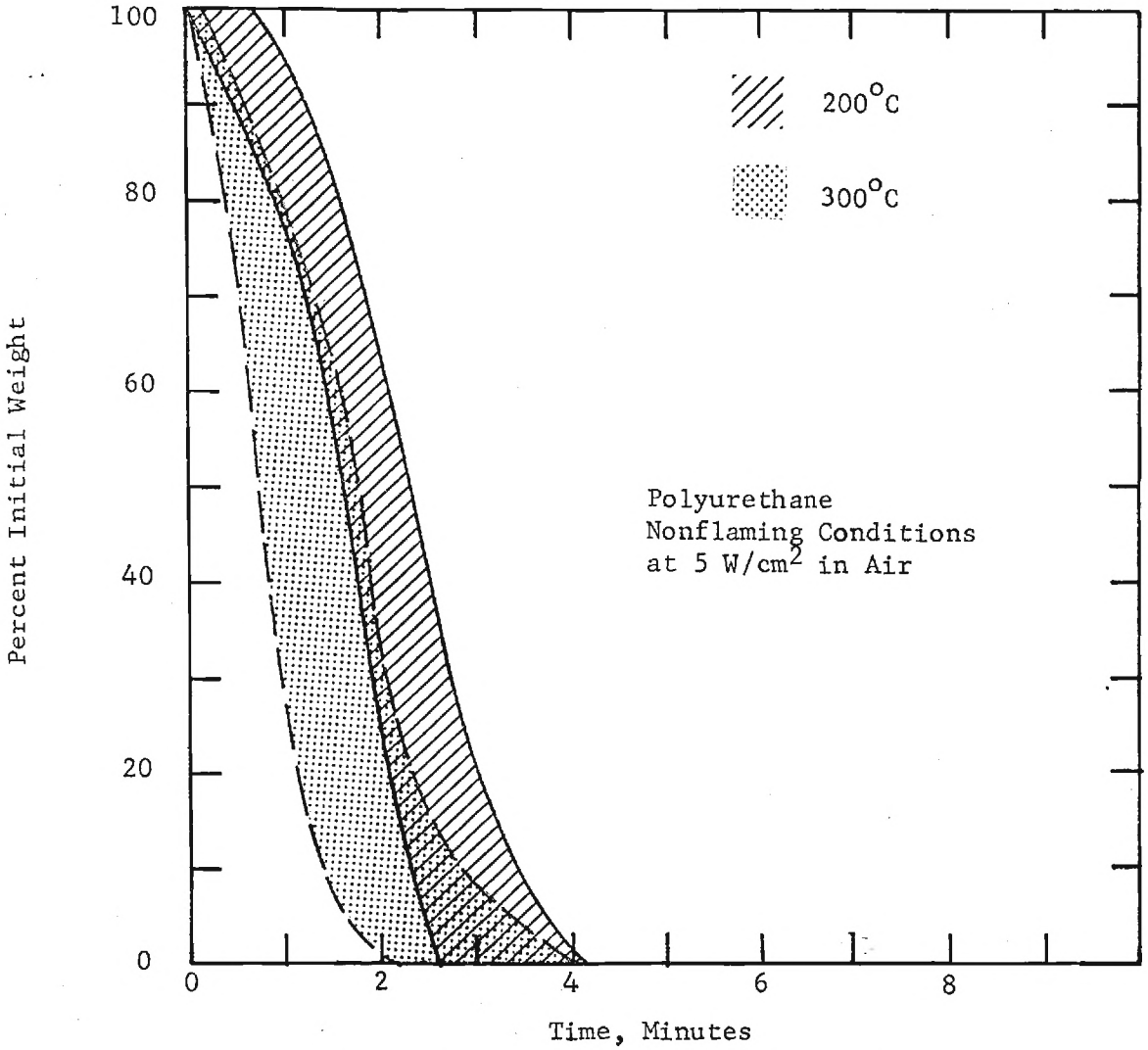

Figure 9. Comparison of Urethane Sample Weight Loss Behavior at 200°C and 300°C.

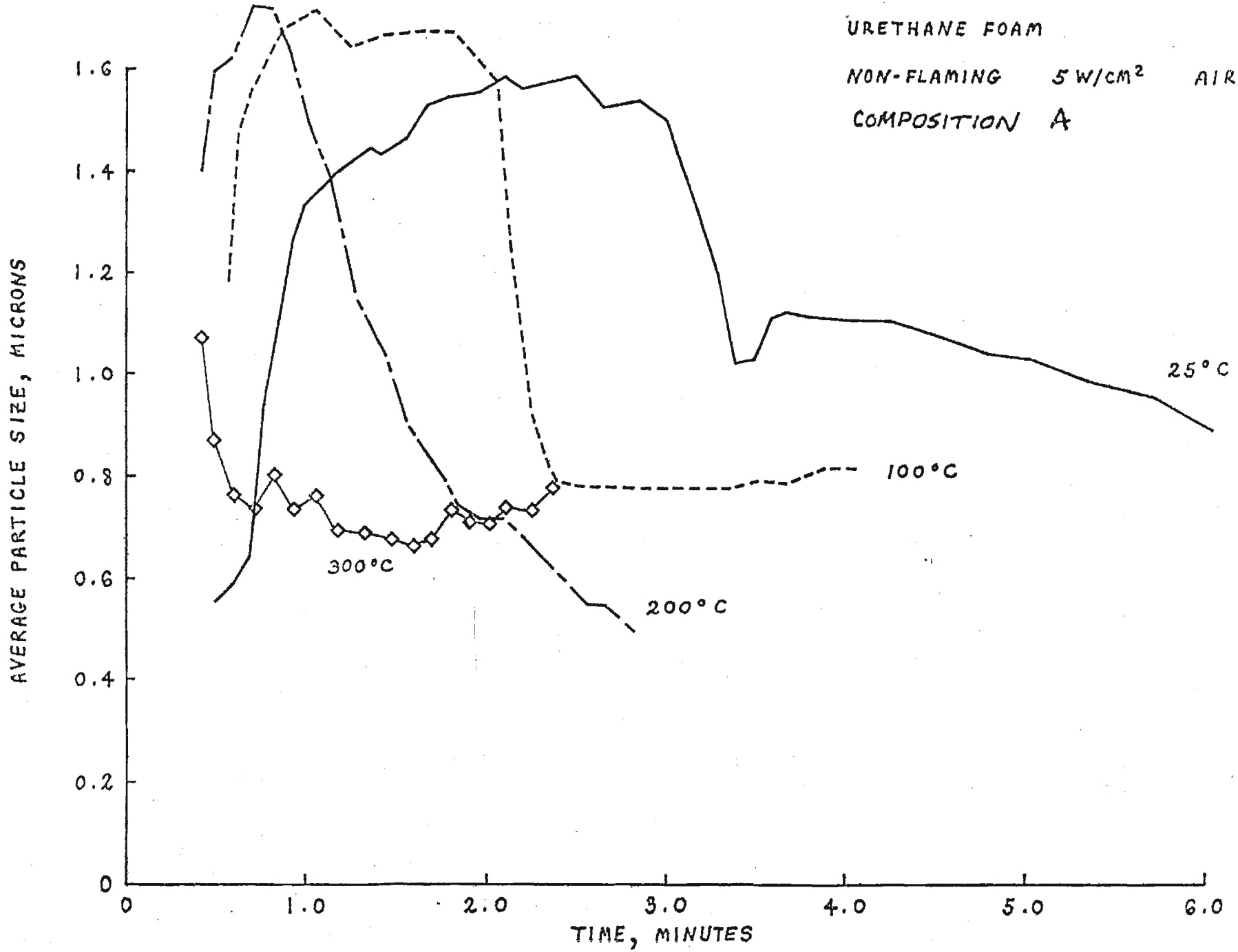

Figure 10. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-

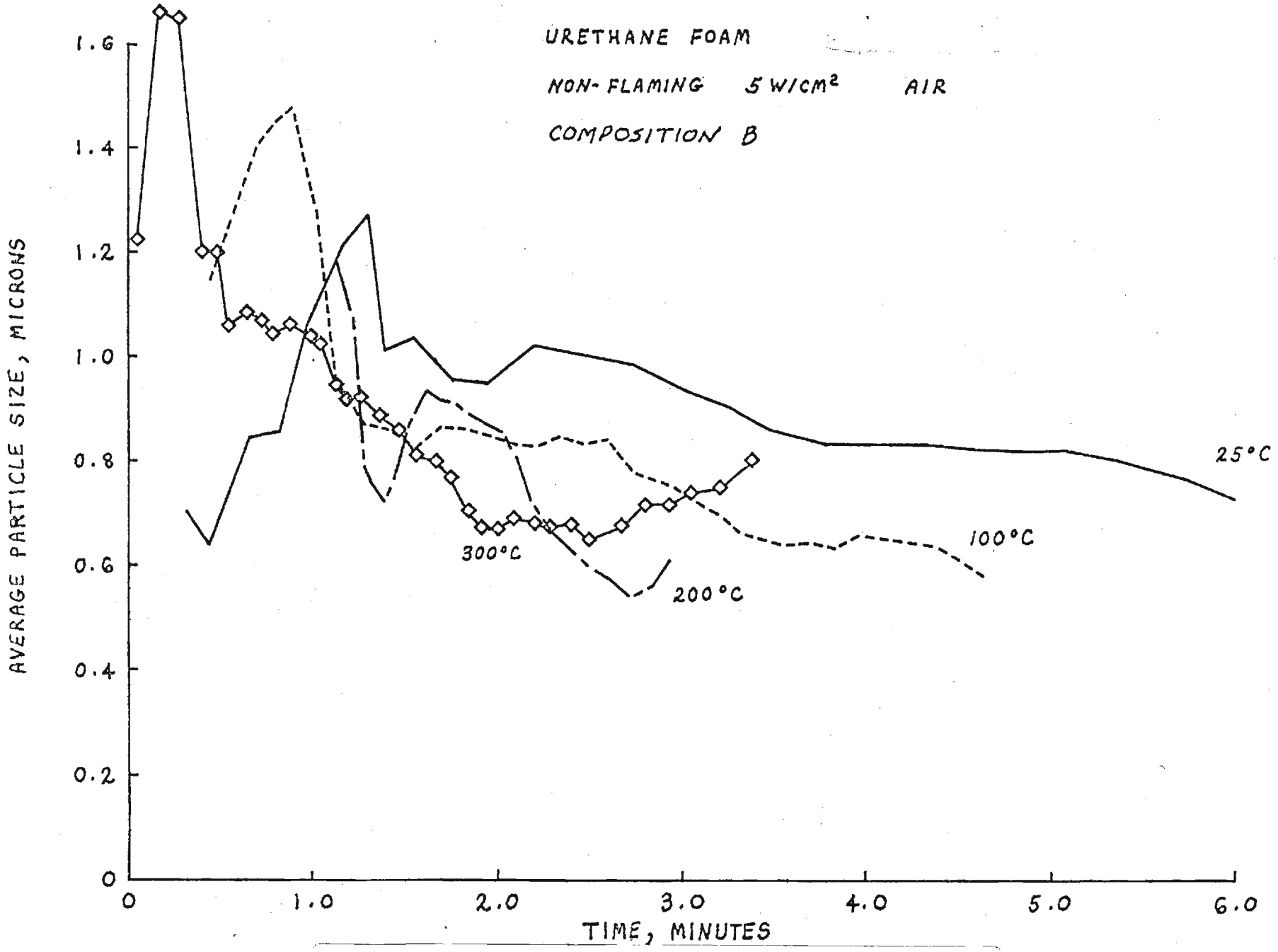

Figure 11. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

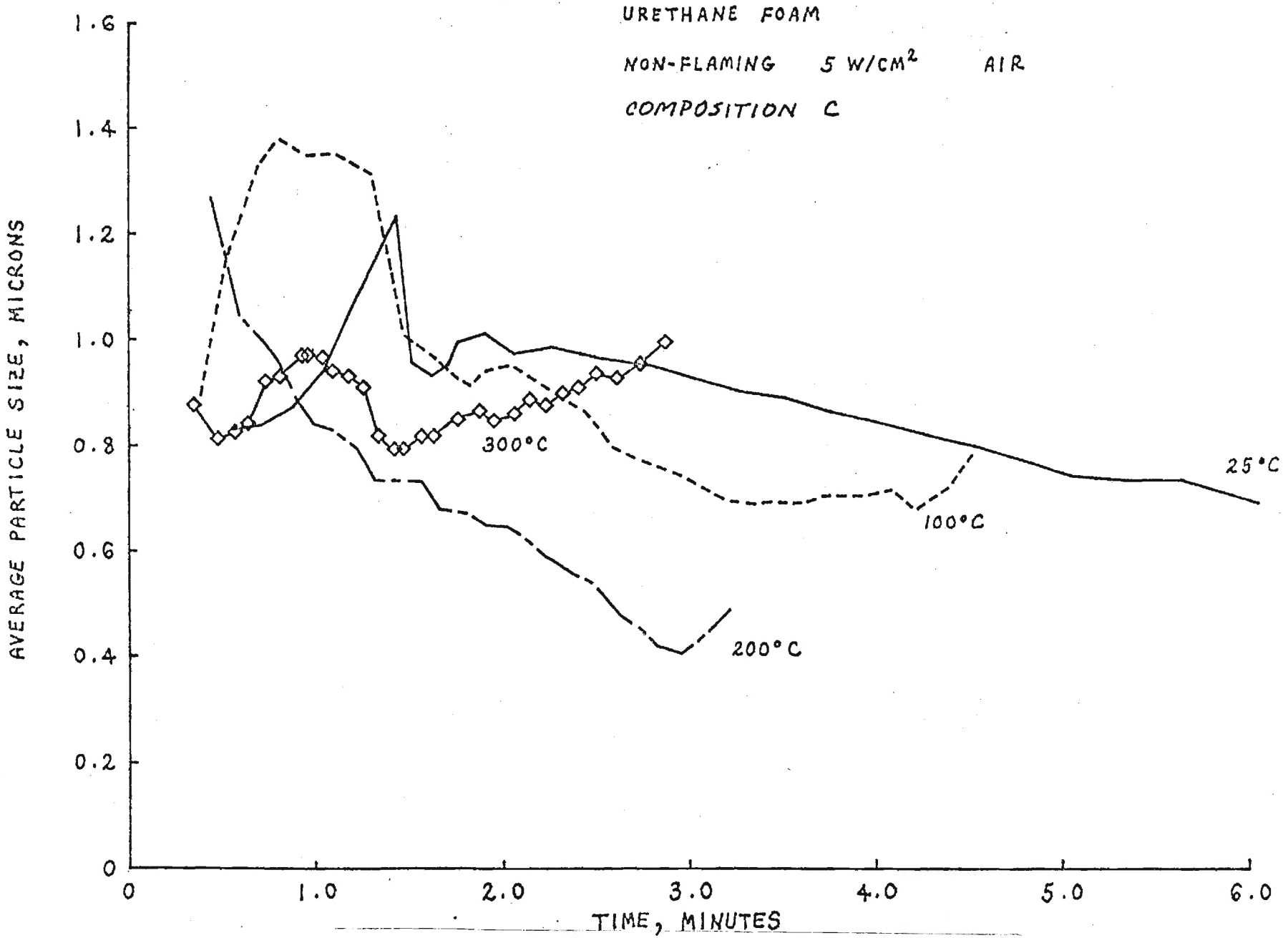

Figure 12. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

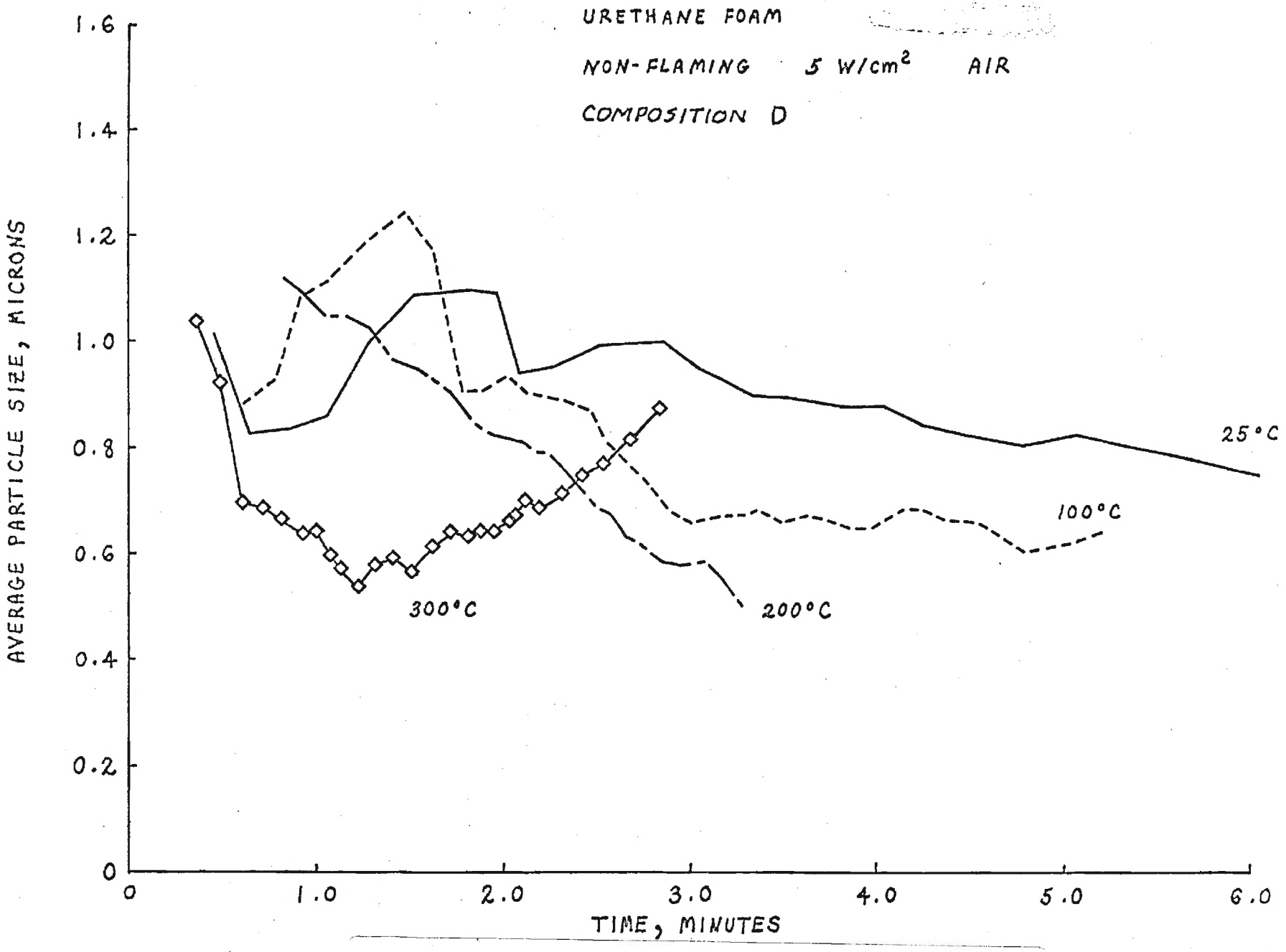

Figure 13. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

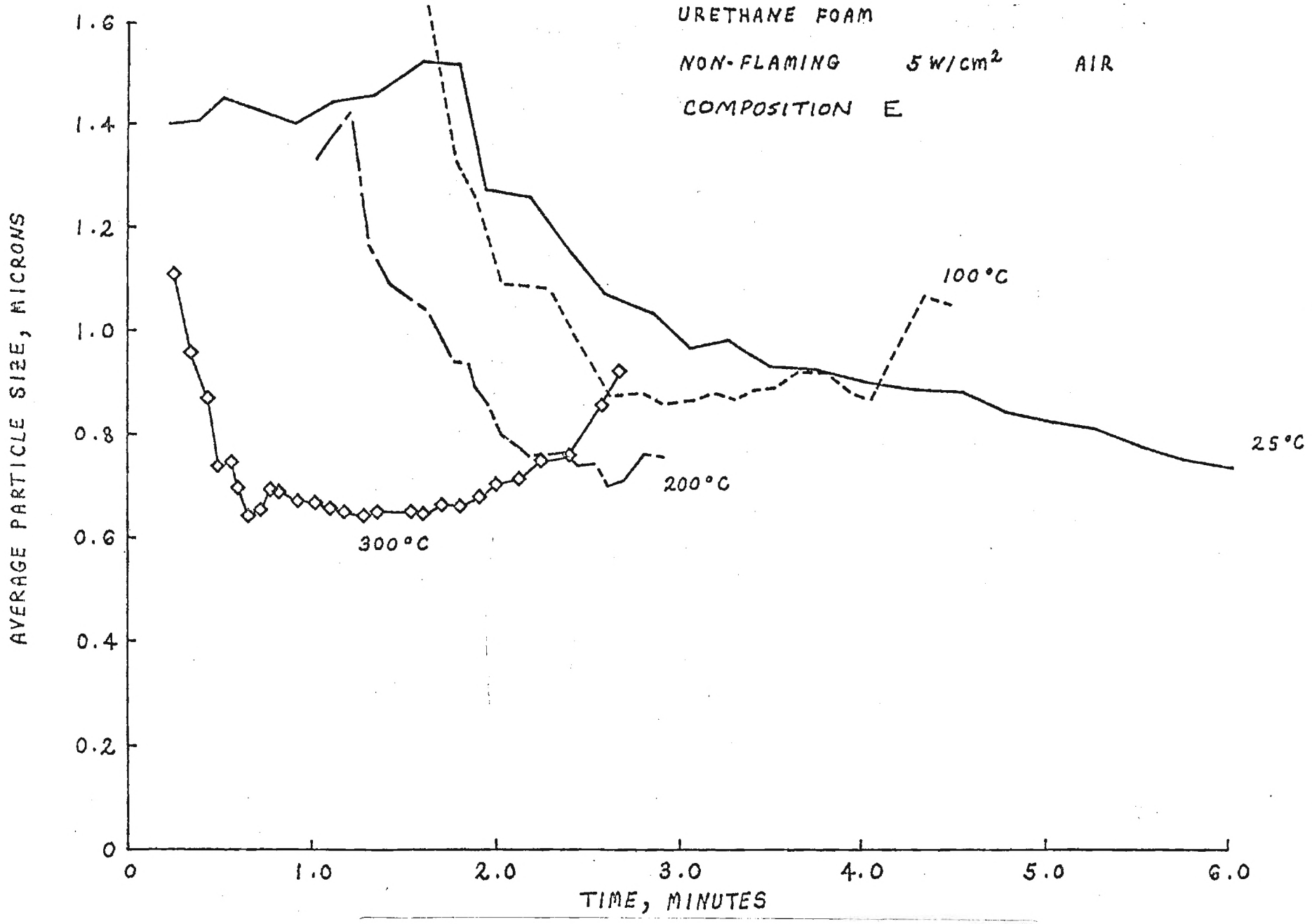

Figure 14. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Nonflaming Polyurethane

Composition B and at 300°C for Composition C.

Optical density behavior during high temperature tests are presented in Figures 15 through 19. Examination of these figures shows that, in general, increasing the environmental temperature results in a reduction in overall optical density levels, where the maximum optical densities are reduced considerably for each temperature increase. Of particular interest is the fact that optical density levels for all tests conducted at 300°C were negligible, and thus do not appear in Figures 15 through 19.

CHEMICAL ANALYSIS OF PARTICULATES

Work on the preseparation of the complex organic mixtures found in the collected particulates has continued. By repetitive collection of fractions eluted from a high pressure liquid chromatograph (column: μ Bondapak C_{18} ; solvent: MeOH/H_2O 75/25) it has been possible to isolate sufficient material for subsequent injection into the gas chromatograph as six separate fractions. By this means, good gas chromatographic separation of the first four fractions has been achieved. Later fractions contain mainly high molecular weight polymeric material which is not suitable for gas chromatographic separation. Direct mass spectral identification of the g.c. peaks has proved difficult because of the presence of homologous series of compounds and of complex isomeric mixtures. Improved gas chromatographic separations, comparison of g.c. retention times and mass spectra of authentic compounds with the unknowns, and possibly I.R. and U.V. absorption spectra will be used to help with compound identification.

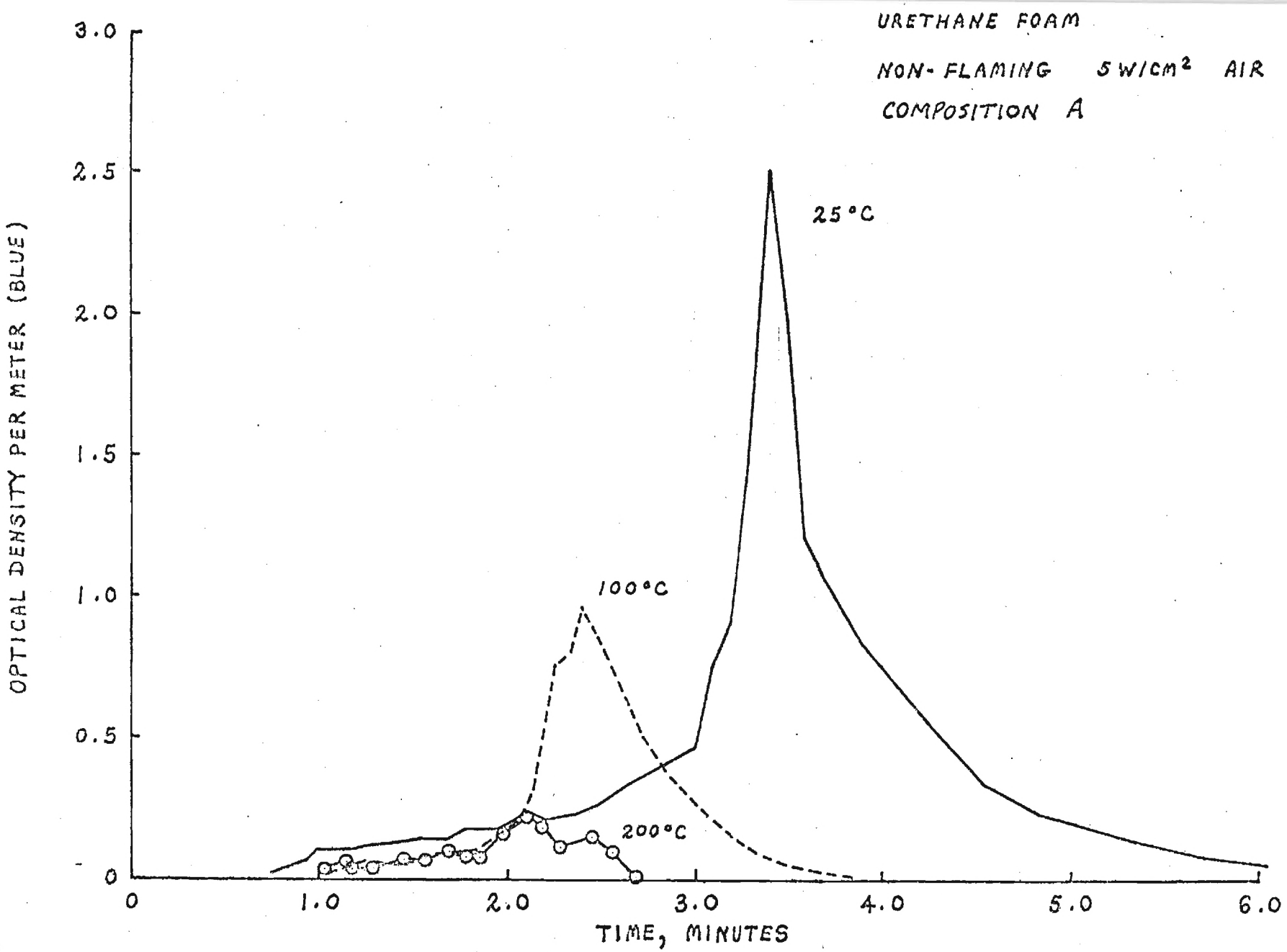

Figure 15. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane.

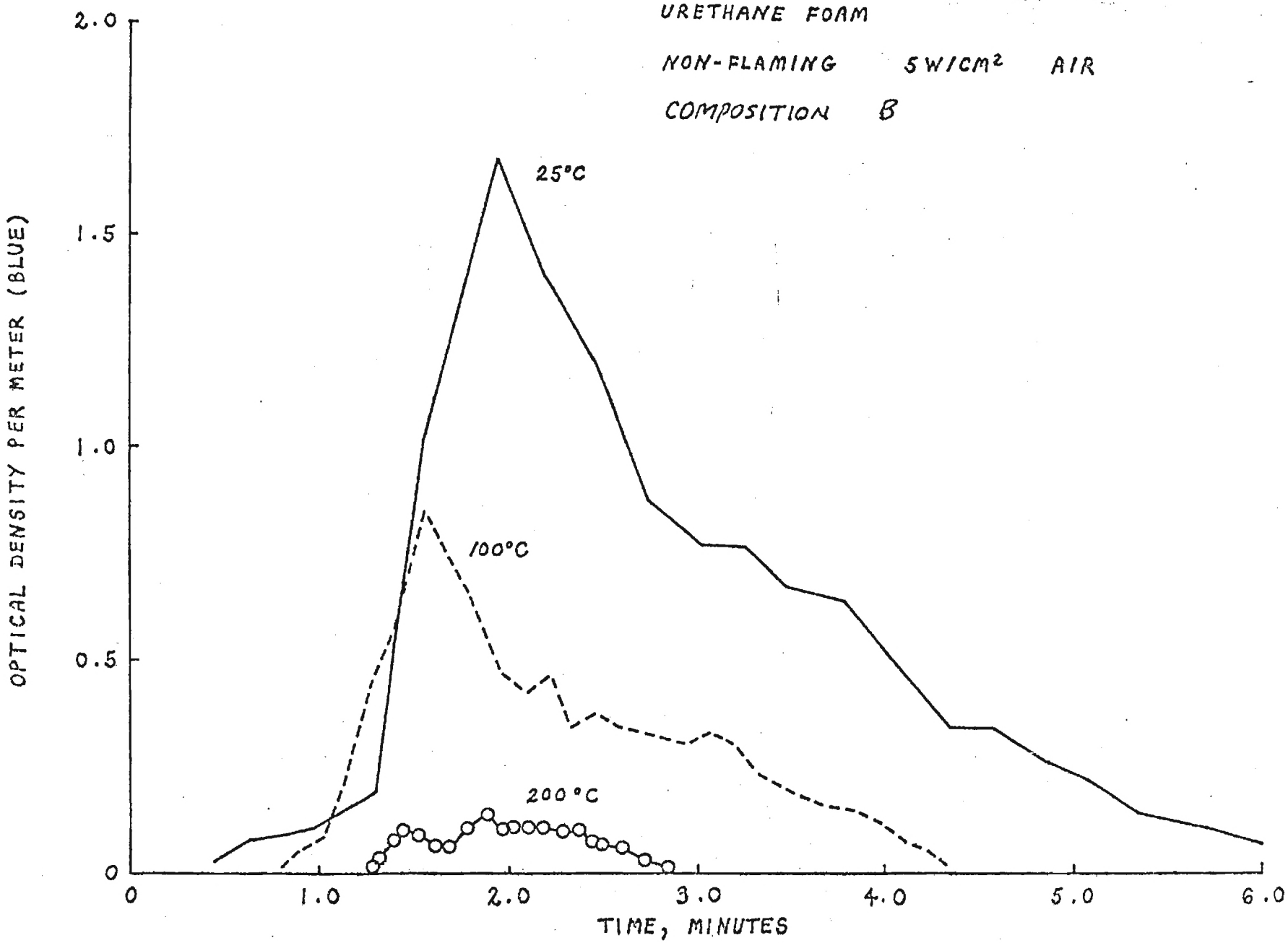

Figure 16. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane.

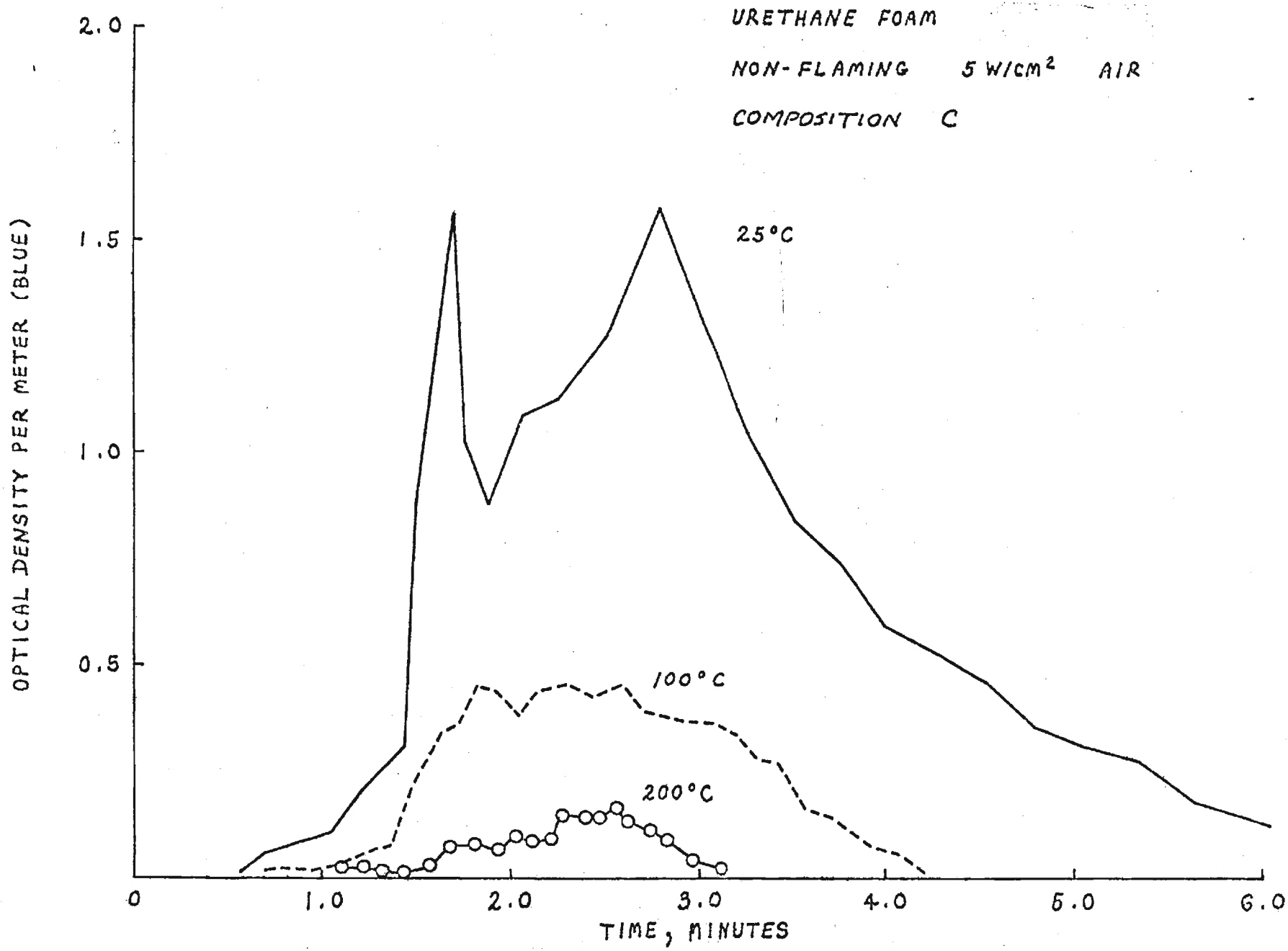

Figure 17. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

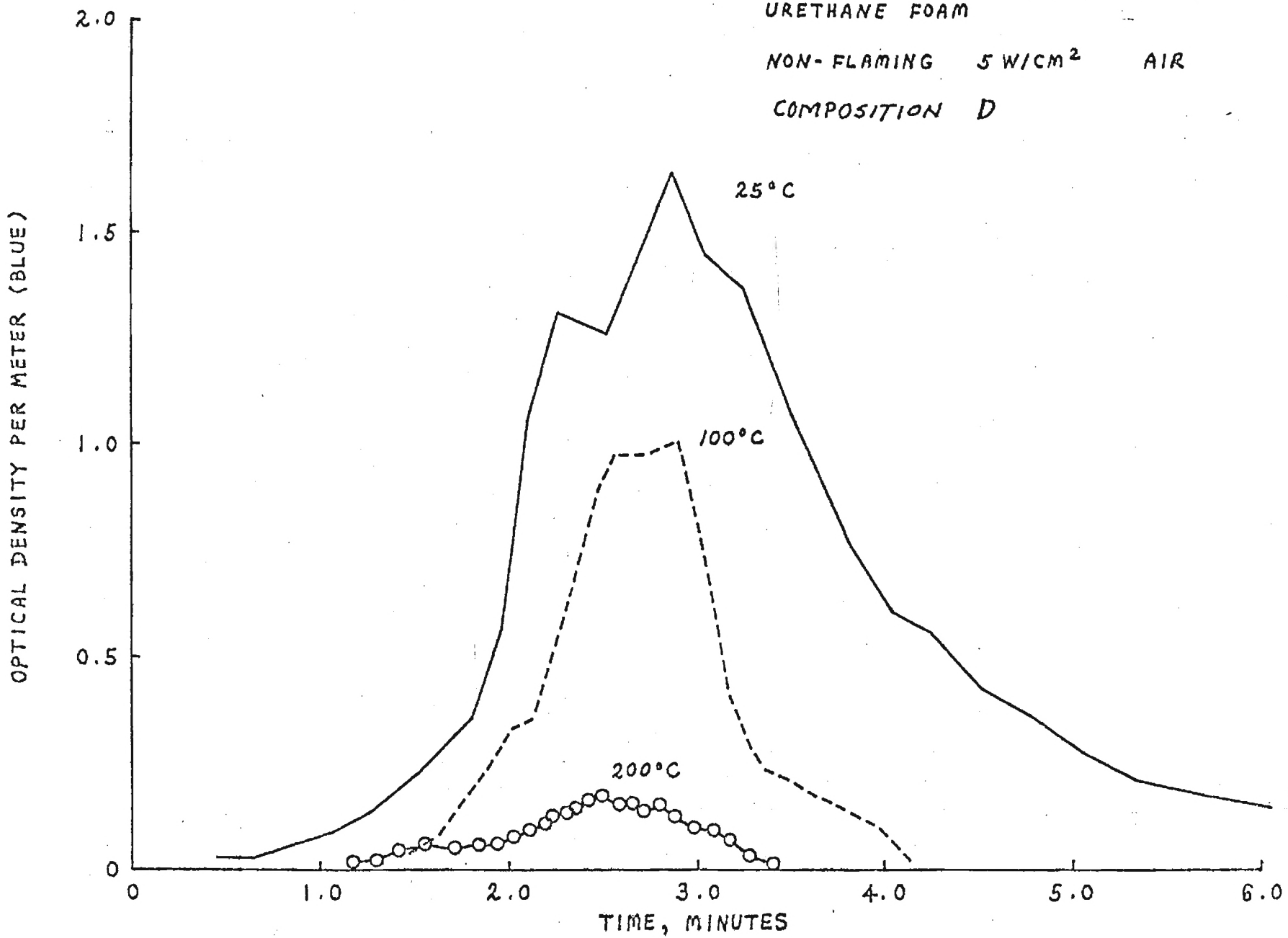

Figure 18. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

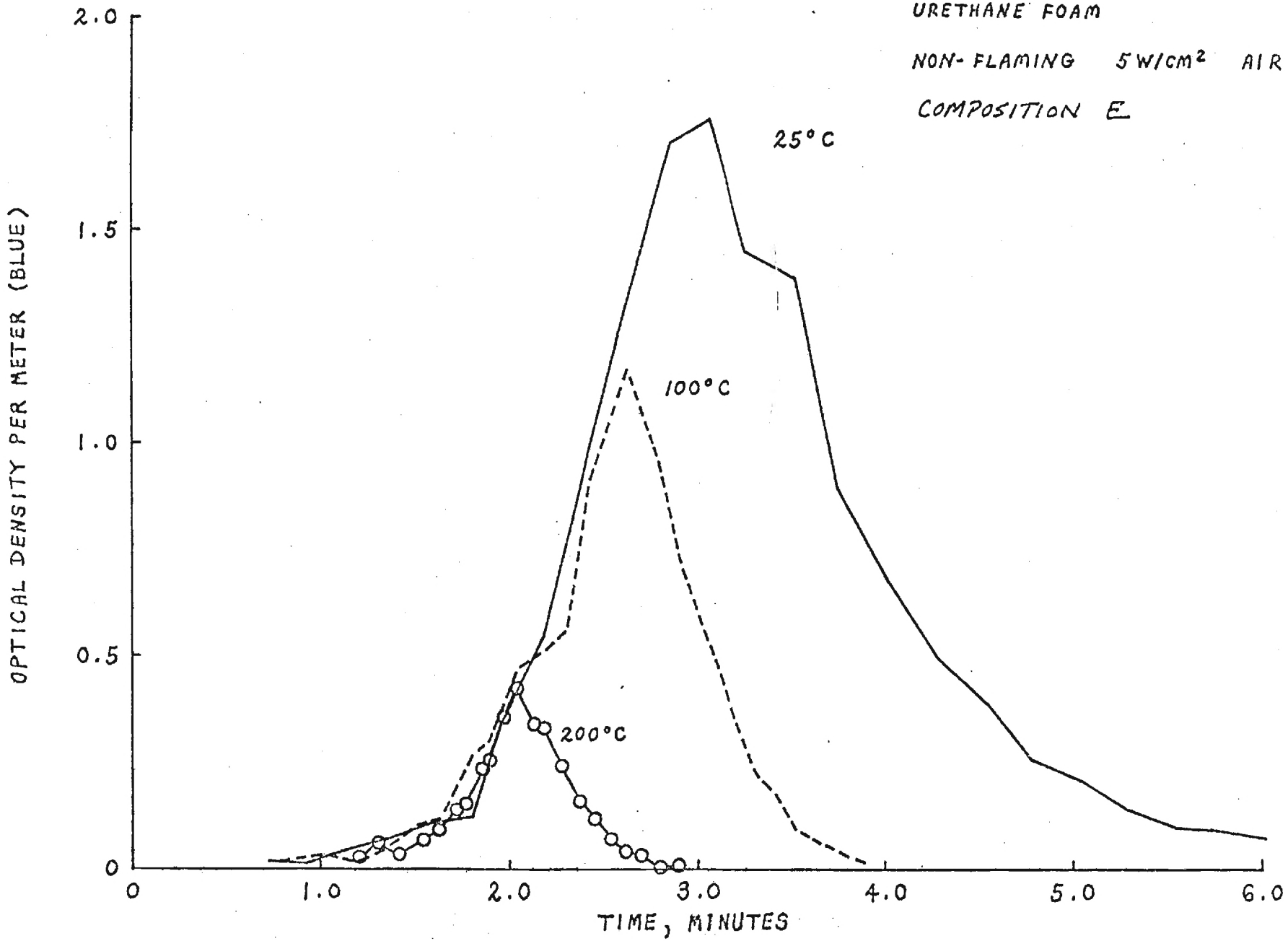

Figure 19. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

APPENDIX

POLYURETHANE SAMPLE COMPOSITIONS

FLEXIBLE POLYURETHANE FOAM

FORMULATIONS - PARTS BY WEIGHT

COMPOSITION	A	B	C	D	E
Poly-G® 3030 PG	100.0	100.0	100.0	100.0	100.0
TDI 80	51.3	51.3	51.3	51.3	51.3
Water	4.0	4.0	4.0	4.0	4.0
Thermolin® 101	-	8.0	-	-	-
HB-32	-	-	8.0	-	-
FR-2	-	-	-	-	8.0
2XC20	-	-	-	8.0	-
L-5710	1.0	1.0	1.0	1.0	1.0
-C-2	0.250	0.250	0.250	0.225	0.225
Dabco 33 LV	0.300	0.300	0.300	0.300	0.300

CHEMICALS

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Manufacturer & Name	Chemical Compound	% Analysis P	% Analysis Cl	% Analysis Br
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Stauffer FR 2	Tris(2,3 Dichloro Propyl) Phosphate	7.2	49.1	-
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INVESTIGATION OF THE PROPERTIES OF THE COMBUSTION PRODUCTS GENERATED BY FIRE-RETARDED POLYURETHANES

B. T. Zinn, Regents' Professor
R. A. Cassanova, Sr. Research Engineer

C. P. Bankston, Research Engineer
E. A. Powell, Assistant Professor
R. F. Browner, Assistant Professor
J. U. Rhee, Post Doctoral Fellow

School of Aerospace Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Final Report of Products Research Committee Project

Number RP-75-1-15-Revised

for the period

October 1, 1976 to September 30, 1977

ABSTRACT

This report describes the research conducted under a Products Research Committee project entitled "Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethanes." The objective of this study is to determine the physical and chemical properties of smoke produced by burning polyurethane foams. Five flexible urethane foams of known composition have been burned under a variety of conditions simulating actual fire situations. Measurements have been made of smoke particle size distributions, total smoke particulate mass generated, smoke mean particle diameter, smoke optical density and sample weight loss. Results show that the measured characteristics are dependent upon the ventilation gas temperature at which samples are burned under both flaming and nonflaming conditions. However, differences between flaming and nonflaming combustion are observed in the trends of the measured quantities as environmental temperature changes. Also, differences in smoke properties are noted among the five urethane compositions considered. Finally, the results of initial room temperature tests of PRC Sample Bank material GM23 are reported.

TABLE OF CONTENTS

I. INTRODUCTION

This report describes the efforts conducted under Products Research Committee research project number [RP-75-1-15 Revised] during the period October 1, 1976 to September 30, 1977. The grant under consideration is entitled "Investigation of the Properties of the Combustion Products Generated by Fire-Retarded Polyurethane". The objective of this study is to determine the physical and chemical properties of the smoke particulates produced when flexible polyurethane foams are burned under different environmental conditions. This program has been directed by Drs. Ben T. Zinn and Robert A. Cassanova in the School of Aerospace Engineering of the Georgia Institute of Technology. Other contributing professional personnel include Drs. E. A. Powell, C. P. Bankston, R. F. Browner and J. U. Rhee.

II. EXPERIMENTAL FACILITIES

The smoke research program described herein has been conducted utilizing the following facilities which have been developed at the School of Aerospace Engineering, Georgia Institute of Technology: (1) A Combustion Products Test Chamber, (2) A Combustion Products Sampling System; (3) An In Situ Optical Aerosol Measurement System; and (4) A Chemical Analysis Laboratory.

The ventilated Combustion Products Test Chamber (CPTC) is capable of simulating a wide variety of environmental conditions that may be encountered in actual fire situations. Specifically, the design of the CPTC permits easy control and measurement of the following variables during the combustion of small samples of materials: (1) The mode of combustion (i.e., flaming vs. smoldering combustion); (2) The sample radiant heating rate (up to 10 watts/cm^2); (3) The sample weight loss during the test; (4) The composition of the ventilating gas surrounding the sample; (5) The temperature of the ventilation gas (up to 650^{o}C) and; (6) An option to test the sample under either vertical or horizontal mounting. A complete description of the CPTC including operating procedures, can be found in References 1 and 2.

During testing,a Combustion Products Sampling System is used to analyze smoke samples that are continuously withdrawn from the gases flowing from the CPTC. Information obtained by the Aerosol Sampling System includes particle size distributions and total particulate mass generated. Some of the collected smoke samples are also retained for chemical analysis. A description of the sampling system can also be found in References 1 and 2.

In addition to the data obtained by sampling techniques, an In Situ Optical Aerosol Measurement System is utilized to make simultaneous mean particle size and concentration measurements. With this optical smoke analysis system measurements of scattered blue light at forward angles of 5^{o} and 15^{o} and measurements of transmitted red and blue laser lights provide time resolved

data describing the average size, volume concentration of the smoke particles, their index of refraction, and their optical density. Details of the optical system are available in References 2 and 3.

An on-line data acquisition system utilizing a Hewlett-Packard 2100 minicomputer is being used for acquiring, reducing and plotting all of the optical and sampling data with the exception of Anderson Sampler (cascade impactor) data which calls for the weighing of the samples collected on the various impaction plates.

Finally, a chemical laboratory containing analytical equipment for the determination of the chemical composition of smoke particulates sampled during tests in the CPTC has been developed. The available equipment includes a high pressure liquid chromatograph, an infrared spectrophotometer, a gas chromatograph equipped with a thermal conductivity detector and a gas chromatograph which is equipped with dual flame ionization detectors and is interfaced to a mass spectrometer. The gas chromatograph/mass spectrometer system is also equipped with a computerized data acquisition and analysis system that records the total-ion chromatograms and the mass spectra.

III. TEST PROTOCOL

A. Sample Compositions

A series of tests has been conducted to determine the physical properties of the smoke produced during the burning of polyurethane samples specifically prepared for testing purposes by one of the leading chemical manufacturers. The chemical compositions of these samples are listed in Table I of this report. Testing with samples of known compositions provides the possibility of relating the measured physical and chemical characteristics of the smoke particulates to the presence of a particular additive in the test sample. In addition, limited testing of a sample obtained from the National Bureau of Standards sample bank was also conducted. This standard fire-retarded sample, designated as GM23, is also being utilized by Dr. Alarie of the University of Pittsburgh in his toxicological studies. It is hoped that some useful correlations will be developed in the future when the results of the Georgia Tech investigations are compared with Dr. Alarie's results. To achieve the desired correlations, the results reported herein for sample GM23 are also being forwarded to Dr. Alarie.

B. Test Conditions and Physical Properties Measured

Each of the five urethane formulations (Table I) was tested under the conditions outlined in Table II. These conditions were selected as representative of a range of environmental extremes which may be encountered in actual fire situations. All samples were mounted in the vertical position and the CPTC ventilation gas was composed of air flowing at 425 liters per minute in all tests. Finally, the average sample dimensions are 75 mm x 75 mm (exposed surface) x 15 mm thick, which correspond to sample weights of 2.5 - 3.0 grams.

For the test conditions characterized by room temperature ($25^{o}C$) ventilation gases, data are available for the following measured quantities: (1) particle

TABLE I.

FLEXIBLE POLYURETHANE FOAM
FORMULATIONS - PARTS BY WEIGHT

COMPOSITION	A	B	C	D	E
Poly-G® 3030 PG	100.0	100.0	100.0	100.0	100.0
TDI 80	51.3	51.3	51.3	51.3	51.3
Water	4.0	4.0	4.0	4.0	4.0
Thermolin® 101	-	8.0	-	-	-
HB-32	-	-	8.0	-	-
FR-2	-	-	-	-	8.0
2XC20	-	-	-	8.0	-
L-5710	1.0	1.0	1.0	1.0	1.0
-C-2	0.250	0.250	0.250	0.225	0.225
Dabco 33 LV	0.300	0.300	0.300	0.300	0.300

CHEMICALS

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Witco C-2	is Stannous Octoate

TABLE I continued

COMMERCIAL NON-REACTIVE

FLAME RETARDANTS

Manufacturer & Name	Chemical Compound	% Analysis P	Cl	Br
Monsanto 2XC20	Chlorinated Diphosphate Ester	10.6	35.2	-
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Olin Thermolin^{R} 101	Tetrakis (2-chloro ethyl) ethylene diphosphate	13.0	31.0	-

TEST NO.	VENTILATION GAS (AIR) TEMPERATURE ^{o}C	TYPE OF COMBUSTION
1	25	FLAMING @ 5W/cm^2
2	25	NONFLAMING @ 2.5 WATTS/cm^2
3	25	NONFLAMING @ 5 WATTS/cm^2
4	25	NONFLAMING @ 10 WATTS/cm^2
5	100	FLAMING @ 5 W/cm^2
6	200	FLAMING @ 5 W/cm^2
7	300	FLAMING @ 5 W/cm^2
8	100	NONFLAMING @ 5 WATTS/cm^2
9	200	NONFLAMING @ 5 WATTS/cm^2
10	300	NONFLAMING @ 5 WATTS/cm^2

Table II. Sample Test Schedule

size distribution; (2) particulate mass generated; (3) the evolution of the mean particle diameter with time; (4) the variation of the smoke optical density (at 458 nm) with time, and (5) the sample mass loss as a function of time. Where test conditions are characterized by high temperature ventilation gases, only in situ optical system data (items 3 and 4 above) are available, in addition to the sample weight loss measurements. The aerosol sampling system instrumentation cannot be operated at elevated temperatures.

IV. RESULTS OF NONFLAMING TESTS OF FLEXIBLE URETHANES OF KNOWN COMPOSITION - PHYSICAL PROPERTIES DATA

A. Low Temperature Tests at 5 W/cm^2 and 10 W/cm^2.

Tests of the five flexible urethane samples under nonflaming conditions in a room temperature (25^{o}C) ventilation gas (air) have been completed. Measurements have been obtained of the characteristics of the smoke produced under nonflaming conditions at 5 W/cm^2 and 10 W/cm^2 radiant flux. The results of these tests are presented in Figures 1 through 14. Also, low temperature tests of the urethane samples at 2.5 W/cm^2 radiant flux were initiated. However, it was found that for the test conditions established in the CPTC (vertical sample mounting and continuous ventilation), the heating rate of 2.5 W/cm^2 results in insufficient sample decomposition to produce measurable quantities of smoke. Thus, no data at the 2.5 W/cm^2 heating rate has been taken.

Figure 1 shows the weight loss data and indicates that all five samples lose 70 to 80% of their initial weight in the first four minutes of exposure to a 5 W/cm^2 radiant heating level. However, compositions C and D appeared to leave a slightly higher percentage of the initial weight as a char than did the other compositions.

Smoke particle size distributions which were obtained with the cascade impactor are shown in Figures 2 and 3. This instrument furnishes the distribution of particulate weight over the aerodynamic size range of 0.43 to 11 microns. The smoke is sampled continuously over the entire test time; thus, the resulting size distribution is an integrated distribution for the entire test. This type of data also gives an indication of the total particulate matter generated by each sample. The data show that there are some differences amongst the five samples in the total particulate weight which is produced by a given sample. Composition A, which is the non fire-retarded sample, pro-

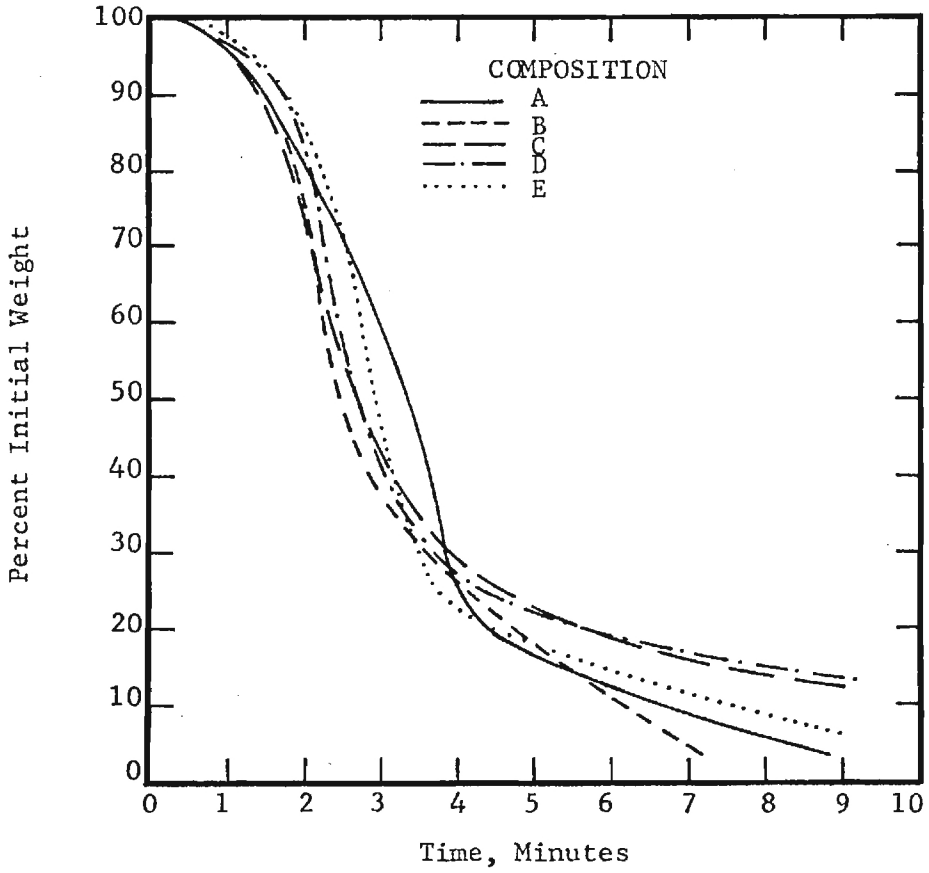


Figure 1. Weight loss of Polyurethanes During Smoldering Combustion at 5 W/cm^2 Radiant Heating in Room Temperature Air

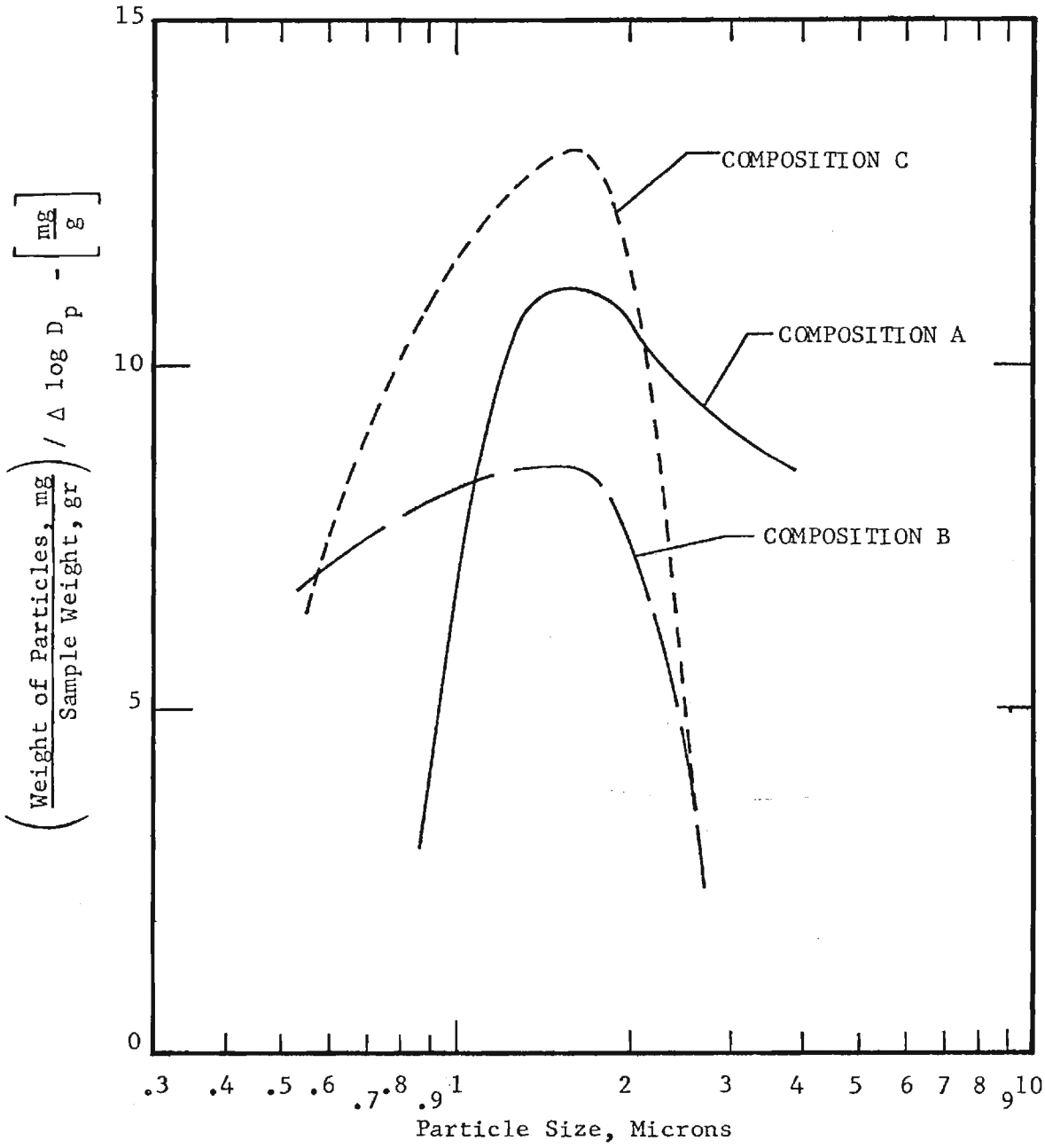


Figure 2. Smoke Particle Size Distribution Integrated Over the Entire Test Time - Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

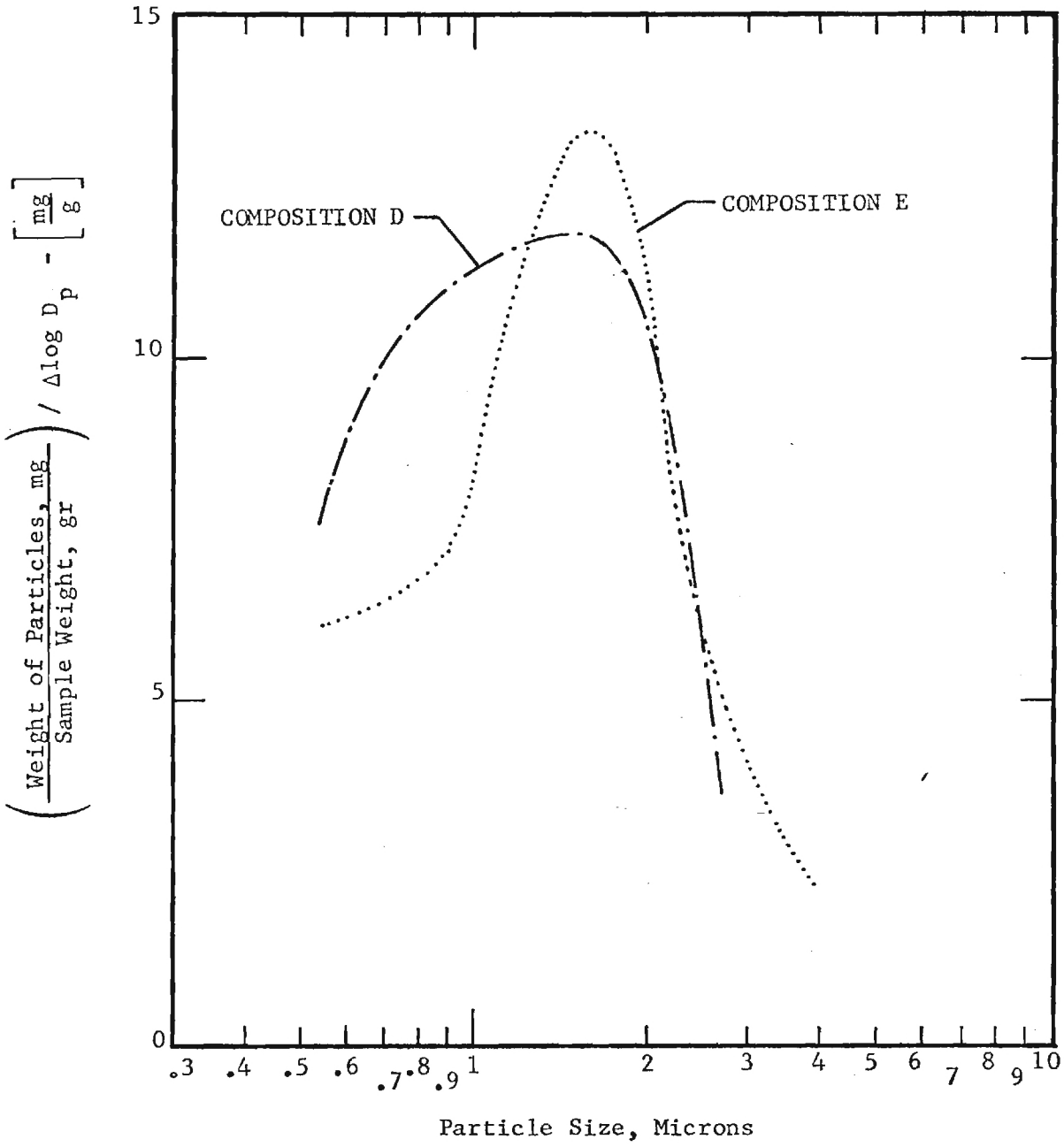


Figure 3. Smoke Particle Size Distribution Integrated Over the Entire Test Time - Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

duced a greater concentration of larger particles and composition E produced a slightly lower concentration of smaller particles than the other compositions.

An indication of the time variation of the average smoke particle size during the tests is shown in Figures 4 and 5. Compositions A and E produced considerably larger particles in the early portion of the test than did the other three compositions. This trend is consistent with the cascade impactor data which was previously described.

Any variation in the particle concentration and size distribution will also cause noticeable changes in the smoke optical density. These comparisons are shown in Figures 6 and 7. The most noticeable result of this data is that the non fire-retarded sample, composition A, produced a higher optical density at a somewhat later time in the test than did the other compositions.

Results of sample weight loss measurements at 10 W/cm^2 are given in Figure 8. Since there were no significant differences in weight loss characteristics among the samples tested at 10 W/cm^2, the data are presented in the indicated band. For comparison purposes, similar data from results obtained at 5 W/cm^2 is also plotted in this figure. These results show that the samples decompose much faster at 10 W/cm^2 when compared to the 5 W/cm^2 radiant flux, and that little measurable sample mass remains at the end of tests at the higher heating rate.

Figures 9 and 10 provide size distributions obtained utilizing the cascade impactor. As observed in the results of tests at 5 W/cm^2, there are differences among the five samples in the total particulate weight which is generated by a given sample. In these data, Compositions C and D produced a lower concentration of larger particles than the other compositions while Compositions A and E

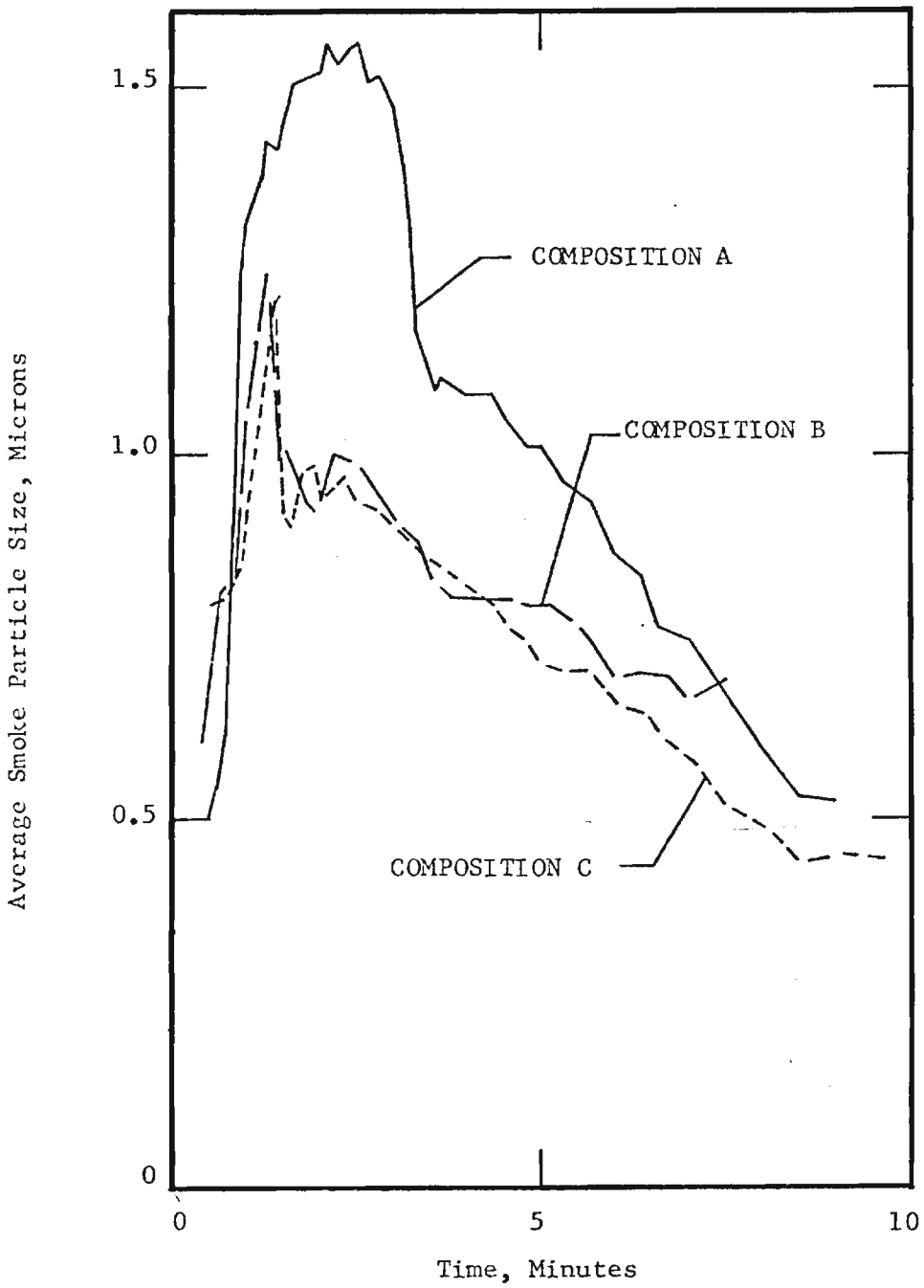


Figure 4. Average Smoke Particle Size Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

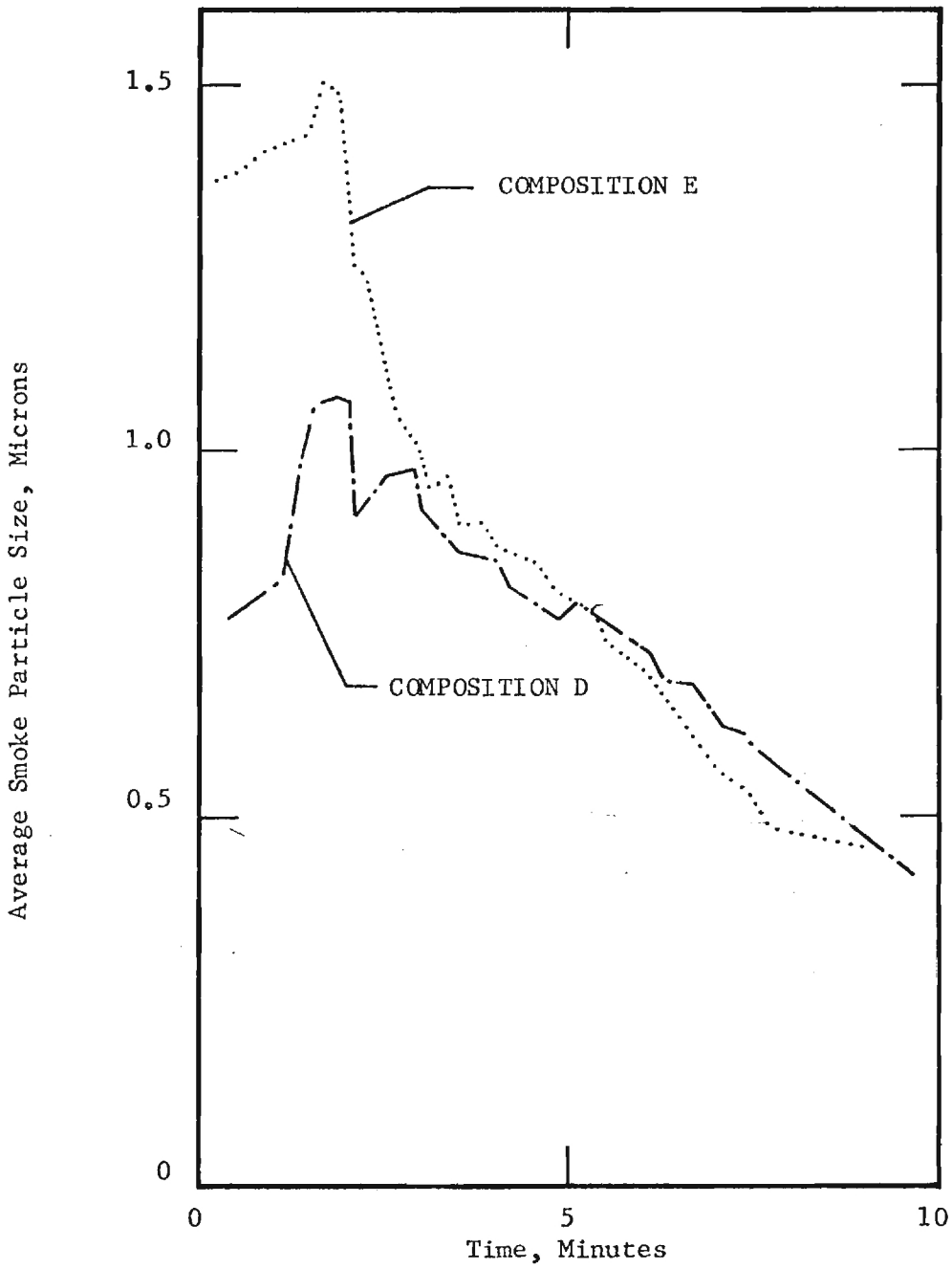


Figure 5. Average Smoke Particle Size Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

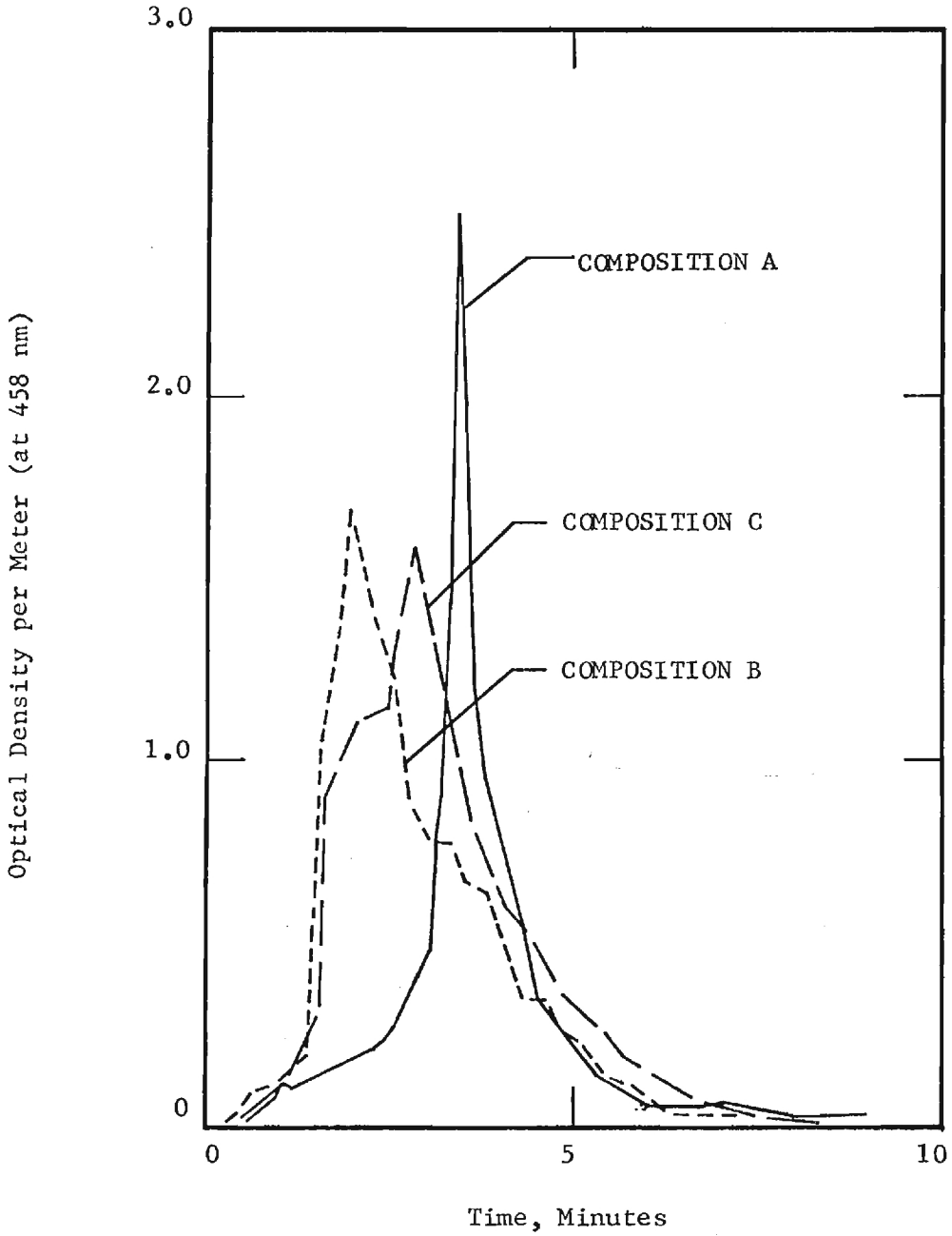


Figure 6. Smoke Optical Density Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

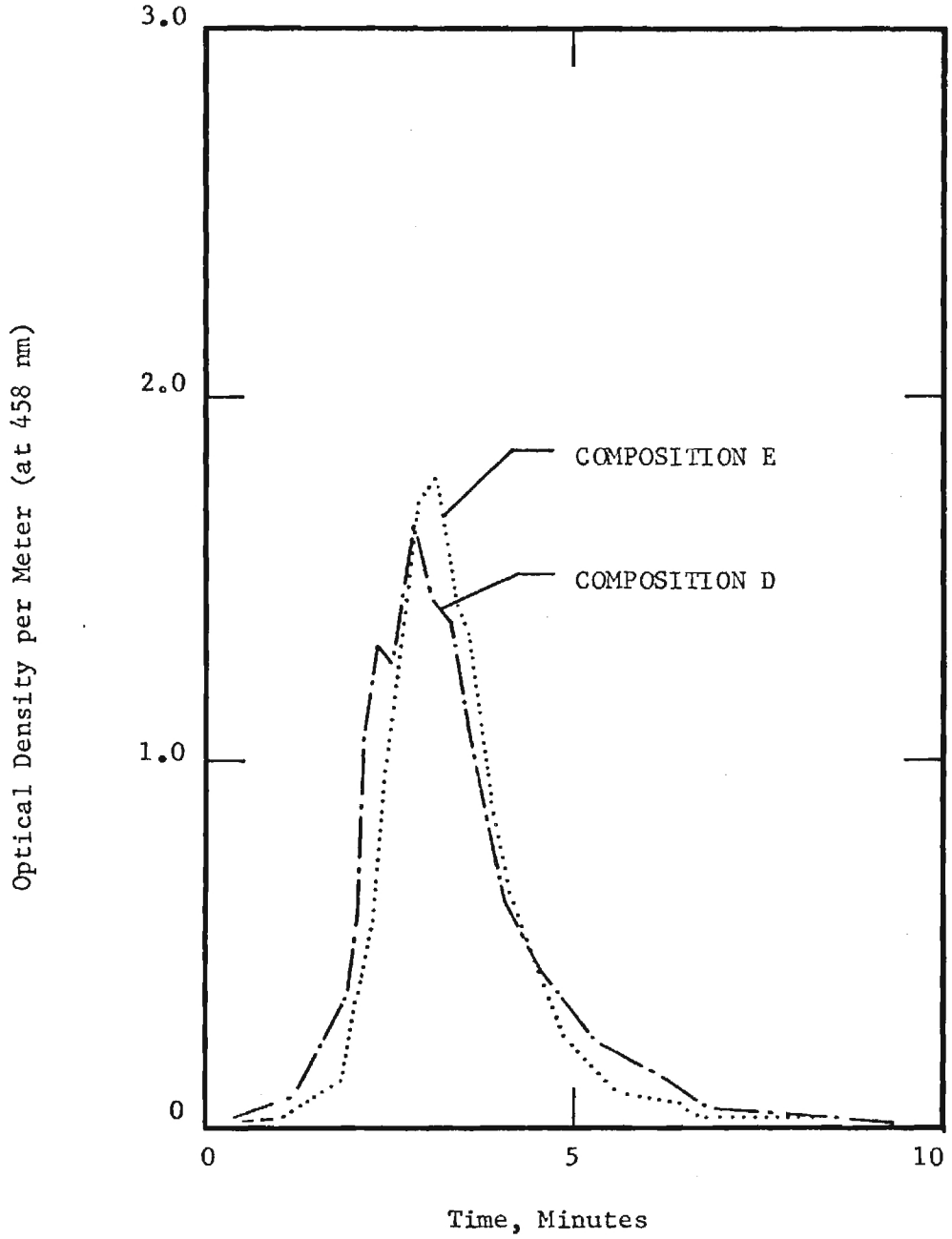


Figure 7. Smoke Optical Density Produced by Flexible Polyurethanes During Smoldering Combustion at 5 W/cm^2 in Room Temperature Air.

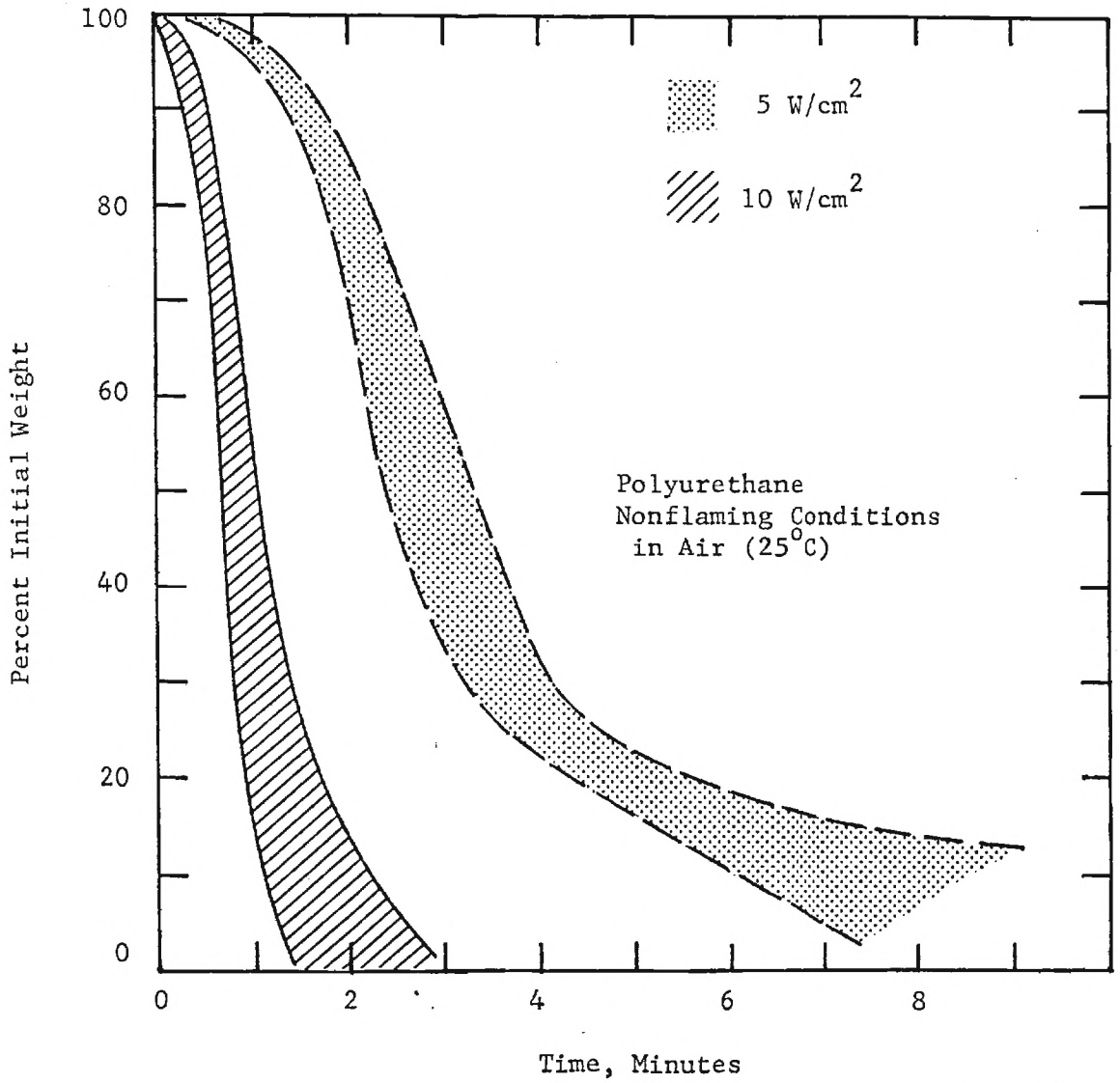


Figure 8. Comparison of Polyurethane Sample Weight Loss Behavior at 5 W/cm^2 and 10 W/cm^2 in Air (25°C)

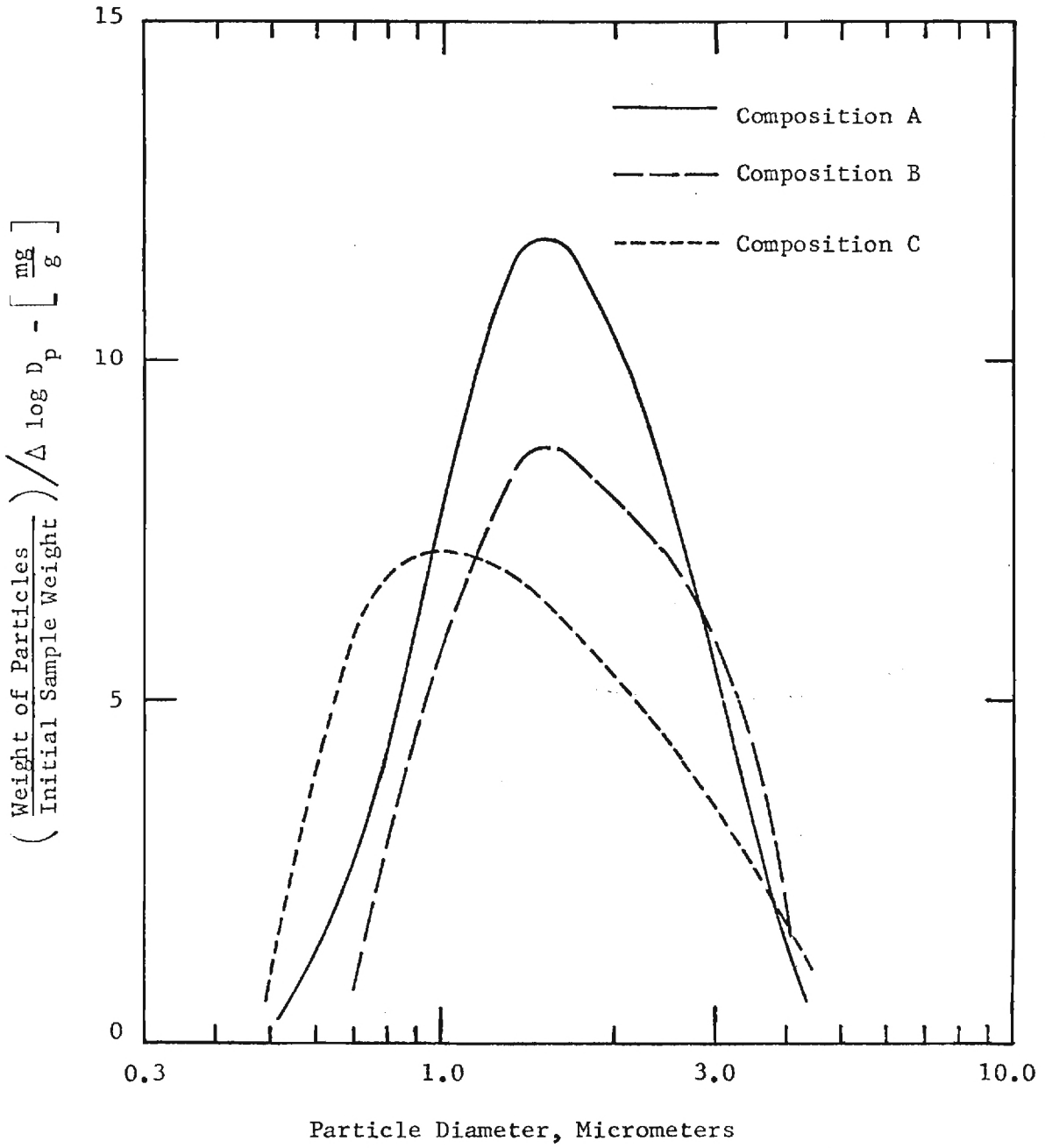


Figure 9. Integrated Smoke Particle Size Distributions for Flexible Polyurethanes - Nonflaming Conditions at 10 W/cm^2 in Air (25^{o}C).

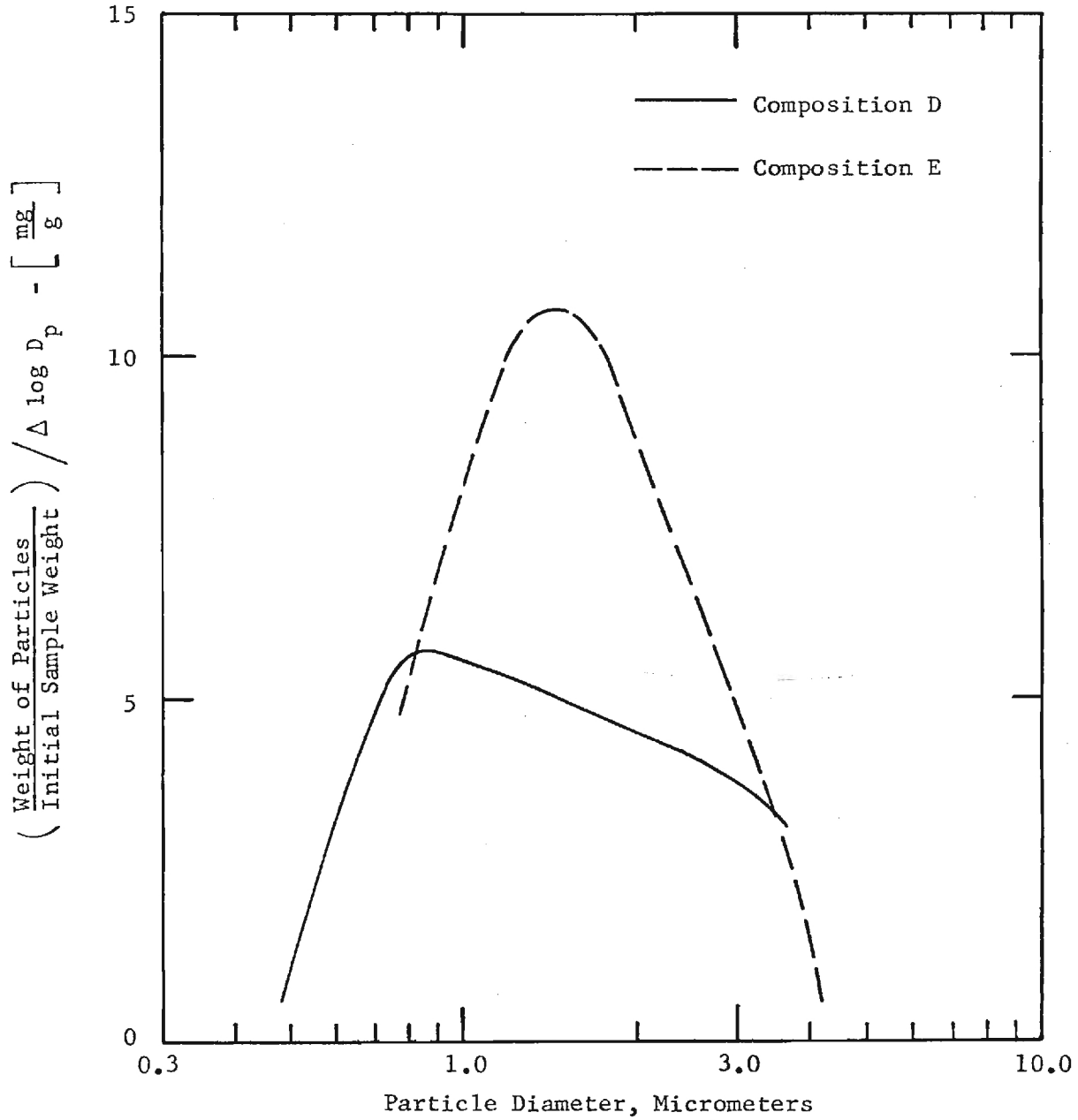


Figure 10. Integrated Smoke Particle Size Distributions for Flexible Polyurethanes - Nonflaming Conditions at 10 W/cm^2 in Air (25°C).

produced the greatest total mass of particles. These data also show that Compositions C and D produced considerably less particulate mass at 10 W/cm^2 when compared to the earlier results obtained at 5 W/cm^2.

Figures 11 and 12 present time-resolved average particle size variations during tests at 10 W/cm^2 radiant heat flux. They show that Compositions C and D produce smaller particles for longer periods than the other compositions, which is consistent with the cascade impactor data. Also, the particle size peak for all samples occurs much earlier at 10 W/cm^2 radiant flux than in the 5 W/cm^2 tests. The smoke optical density behavior shown in Figures 13 and 14 is characterized by peaks at t = 1 minute for all samples; where these peaks appear earlier than the corresponding peaks observed in 5 W/cm^2 tests. The maximum optical densities in 10 W/cm^2 tests were greater for Compositions B and E.

Summary

In the low temperature nonflaming tests of five flexible urethane foams at 5 W/cm^2 and 10 W/cm^2 radiant flux, sample weight loss measurements show no significant differences in weight loss characteristics among the five samples when compared at each of the two heating rates. However, the samples do decompose much faster at 10 W/cm^2 when compared to the 5 W/cm^2 radiant flux. Insofar as smoke particle sizes are concerned, samples A and E generally produced greater quantities of larger particles; where no discernible trend is evident for Samples B, C and D. In most cases particle size distribution peaks are in the 1-2 μm range. Finally, no definite trends are apparent in the smoke optical density and total particulate mass measurements among the five samples tested.

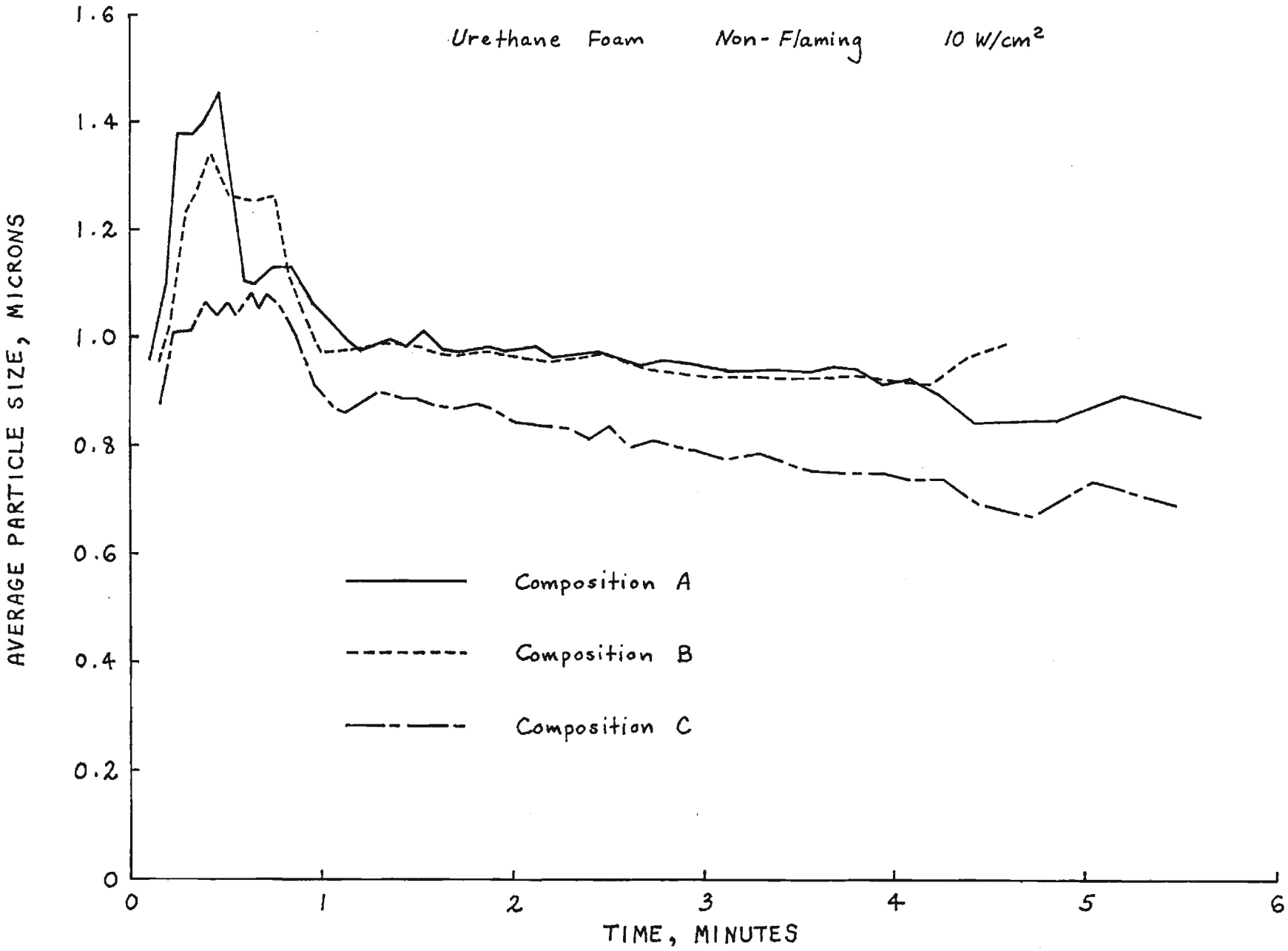


Figure 11. Time Resolved Smoke Particle Size Behavior at 10 W/cm^2 - Nonflaming Polyurethanes

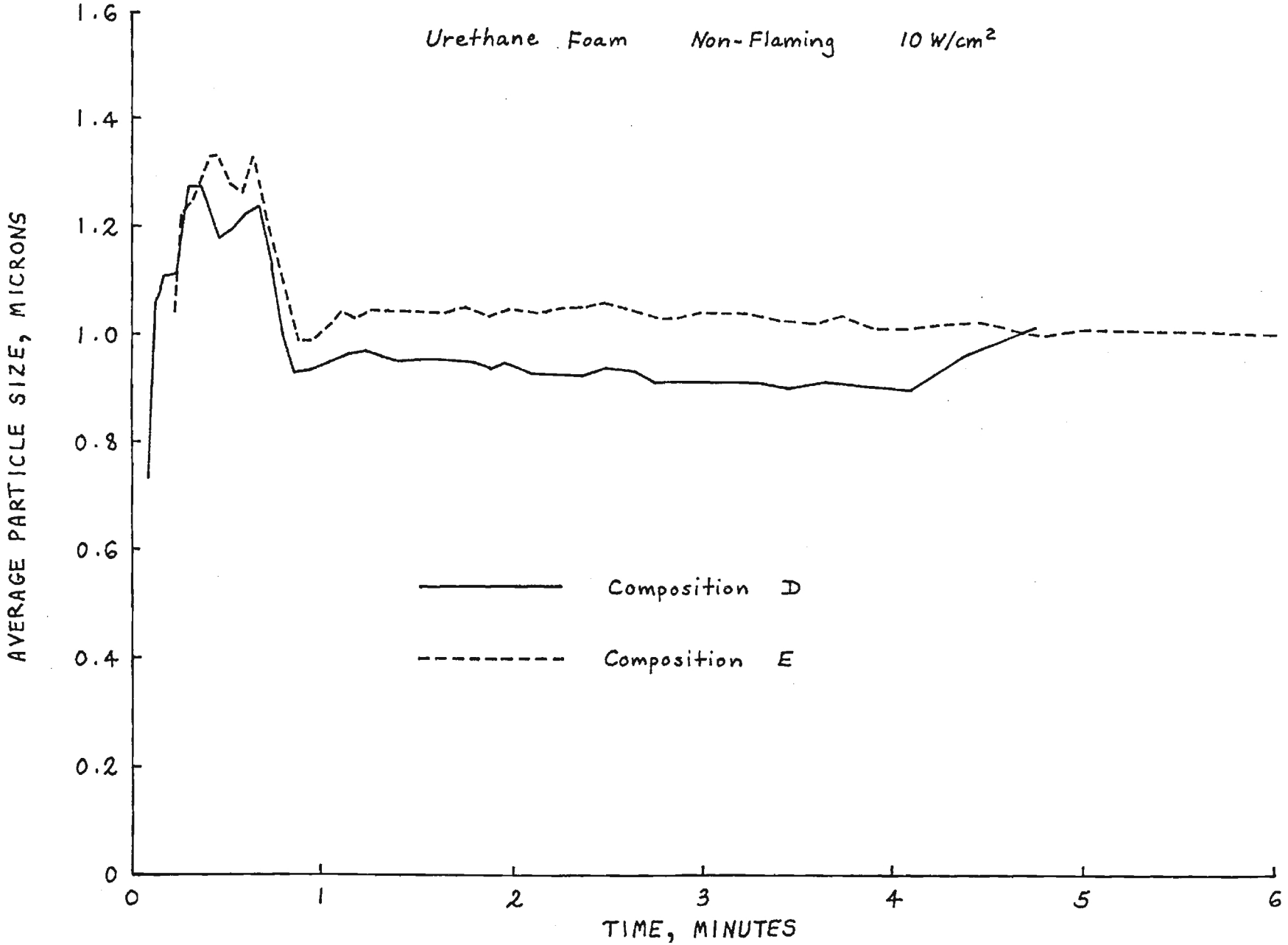


Figure 12. Time Resolved Smoke Particle Size Behavior at 10 W/cm^2 - Nonflaming Polyurethanes

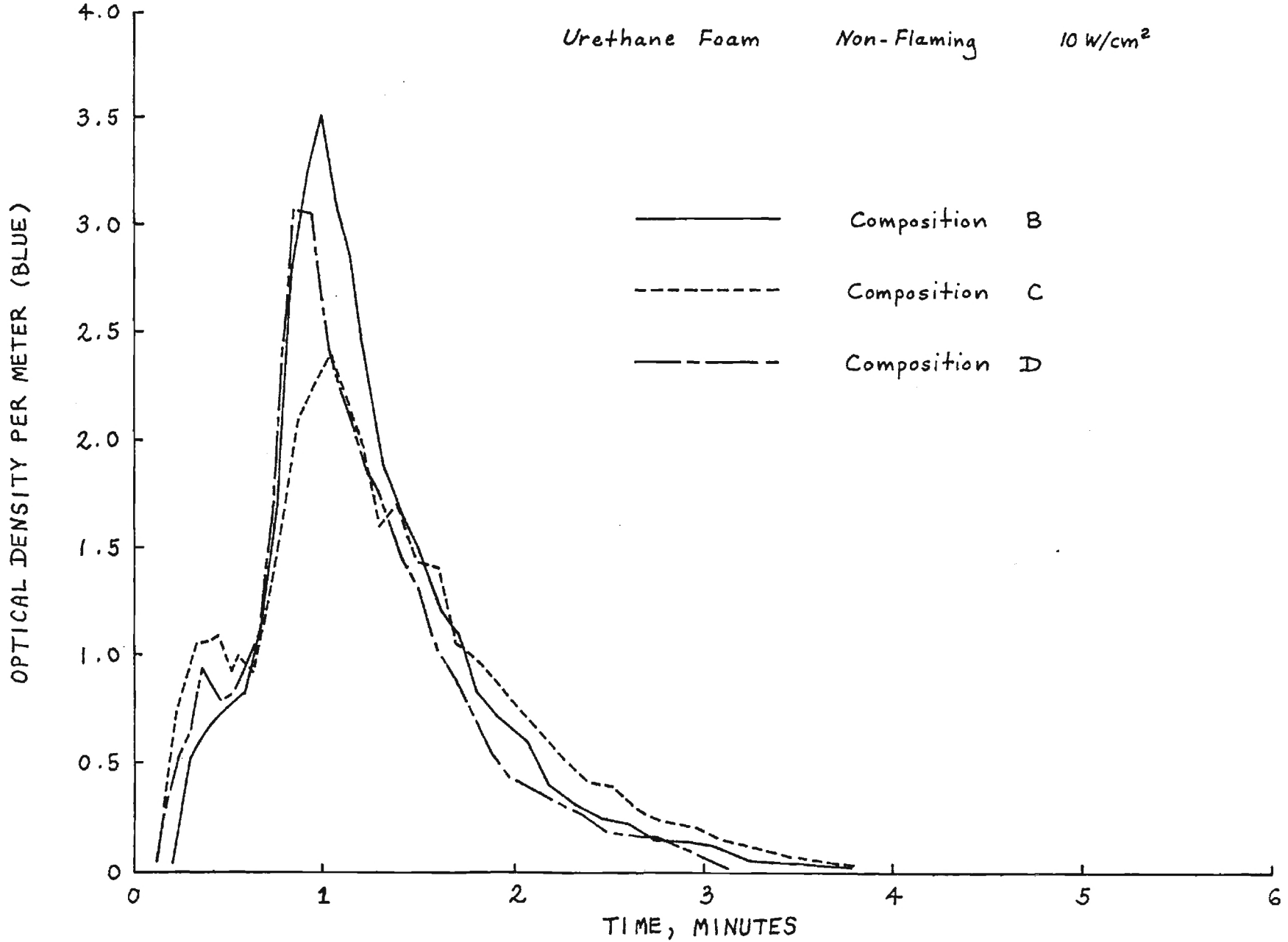


Figure 13. Smoke Optical Density Behavior at 10 W/cm^2 - Nonflaming Polyurethanes

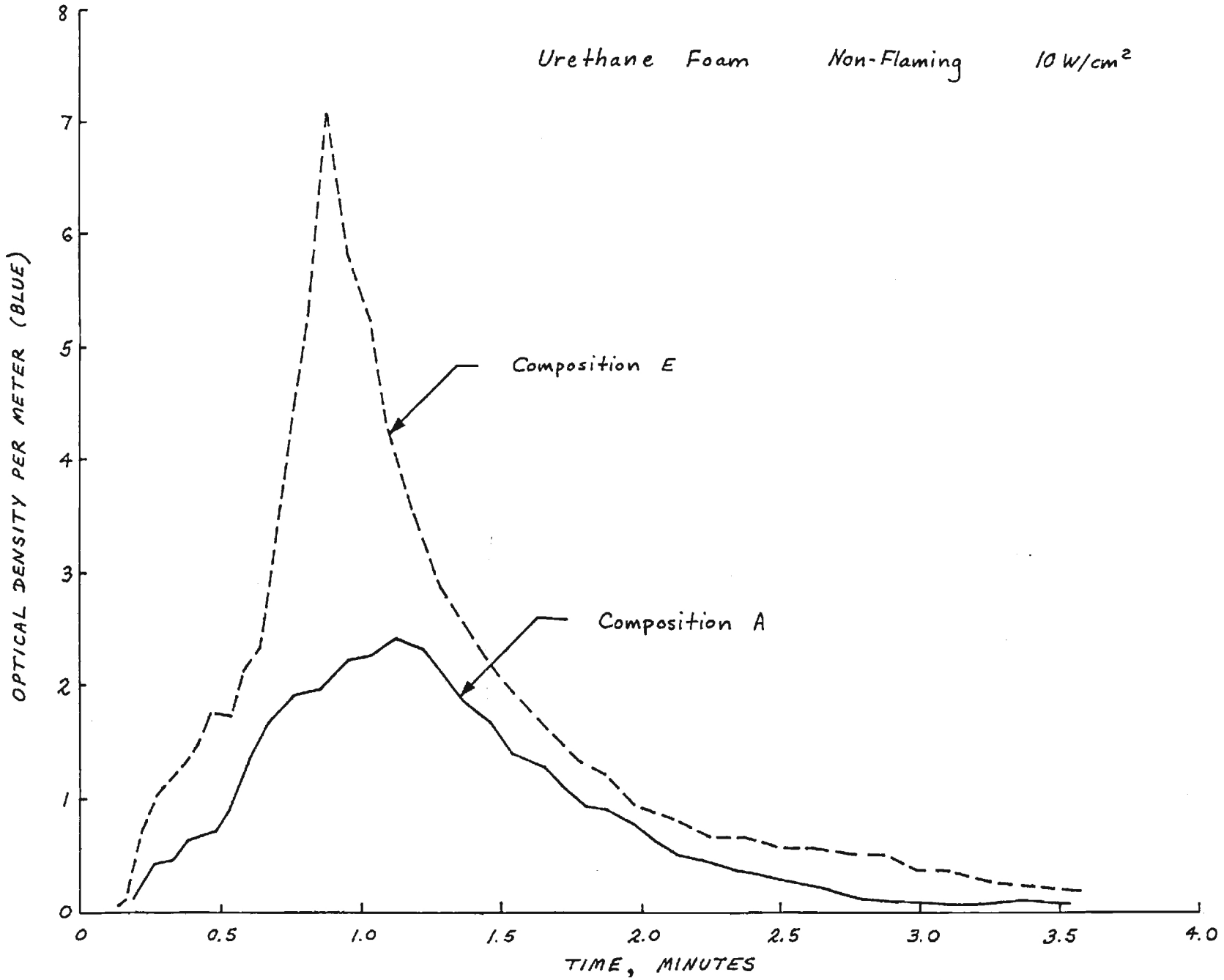


Figure 14. Smoke Optical Density Behavior at 10 W/cm^2 - Nonflaming Polyurethanes

B. High Temperature Tests at 5 W/cm^2.

High temperature tests of the five flexible urethane samples have been conducted according to the test schedule outlined in Table II. Measurements of the physical characteristics of smoke generated by smoldering samples have been taken for ventilation gas (air) temperatures of 100°C, 200°C and 300°C, while the samples were exposed to 5 W/cm^2 radiant flux. As mentioned previously, this series of tests has been limited to in situ optical system and force transducer measurements, since the aerosol sampling system instrumentation cannot be operated at elevated temperatures.

Figures 15 and 16 summarize the weight loss data which have been obtained at high temperatures with the five polyurethane samples. The data are presented in characteristic bands for each ventilation gas temperature, including room temperature (25°C) data. The results show that the effect of increasing the environmental temperature is to increase the rate at which the sample is pyrolyzed and loses weight.

Figures 17-21 describe the time dependence of the smoke particle mean diameter, D_{32}, measured for each of the urethane samples at all ventilation gas temperatures under consideration. The data indicate that for Compositions A, D and E the production of the largest particles occurs earlier in the test as the environmental temperature increases. The results for those three compositions also show that in general, after the maximum particle size is reached, somewhat smaller particles are produced for each increase in ventilation gas temperature. These trends are also observed for Compositions B and C although exceptions are noted at 200°C in the results for Composition B and at 300°C for Composition C.

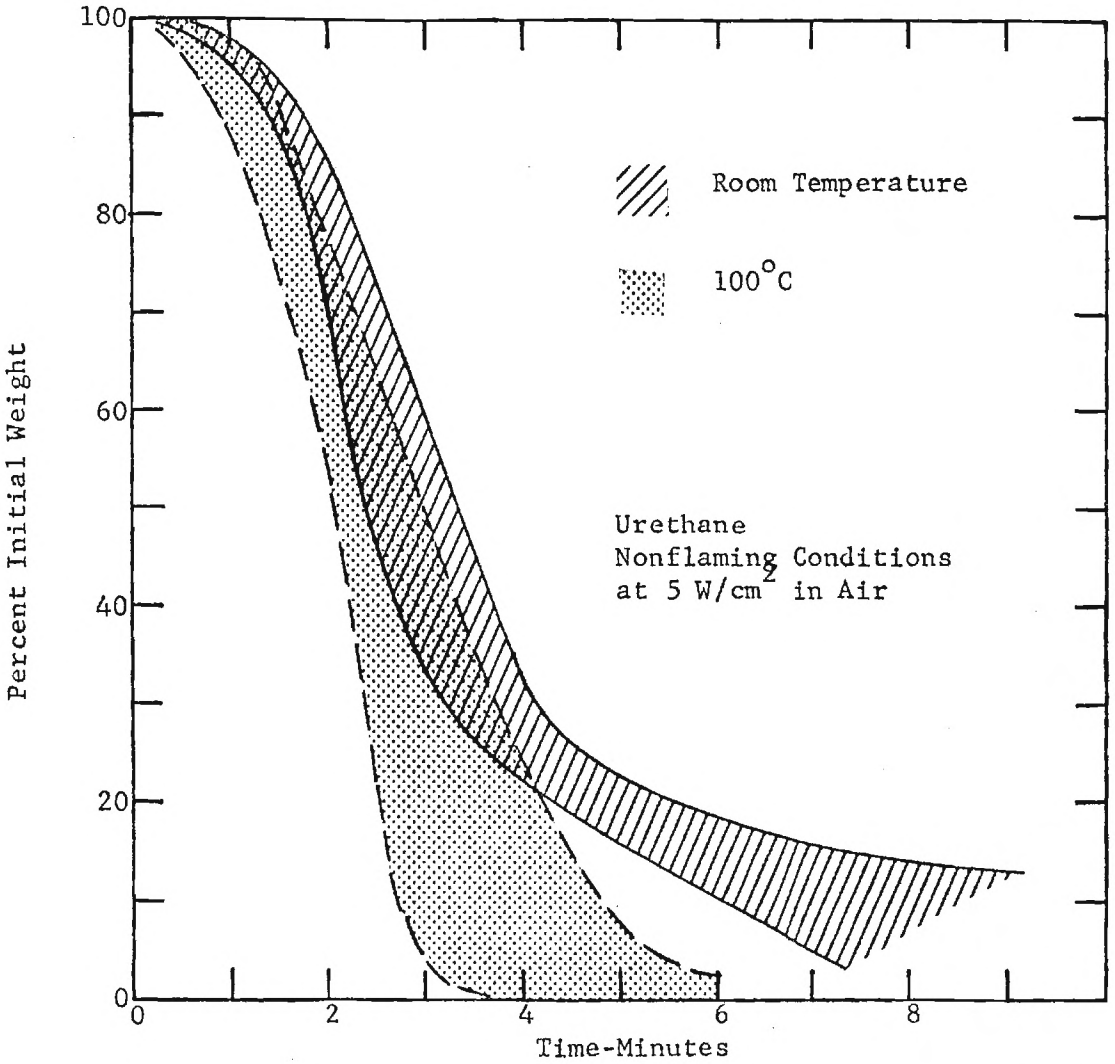


Figure 15. Comparison of Urethane Sample Weight Loss Behavior at 100°C. and Room Temperature

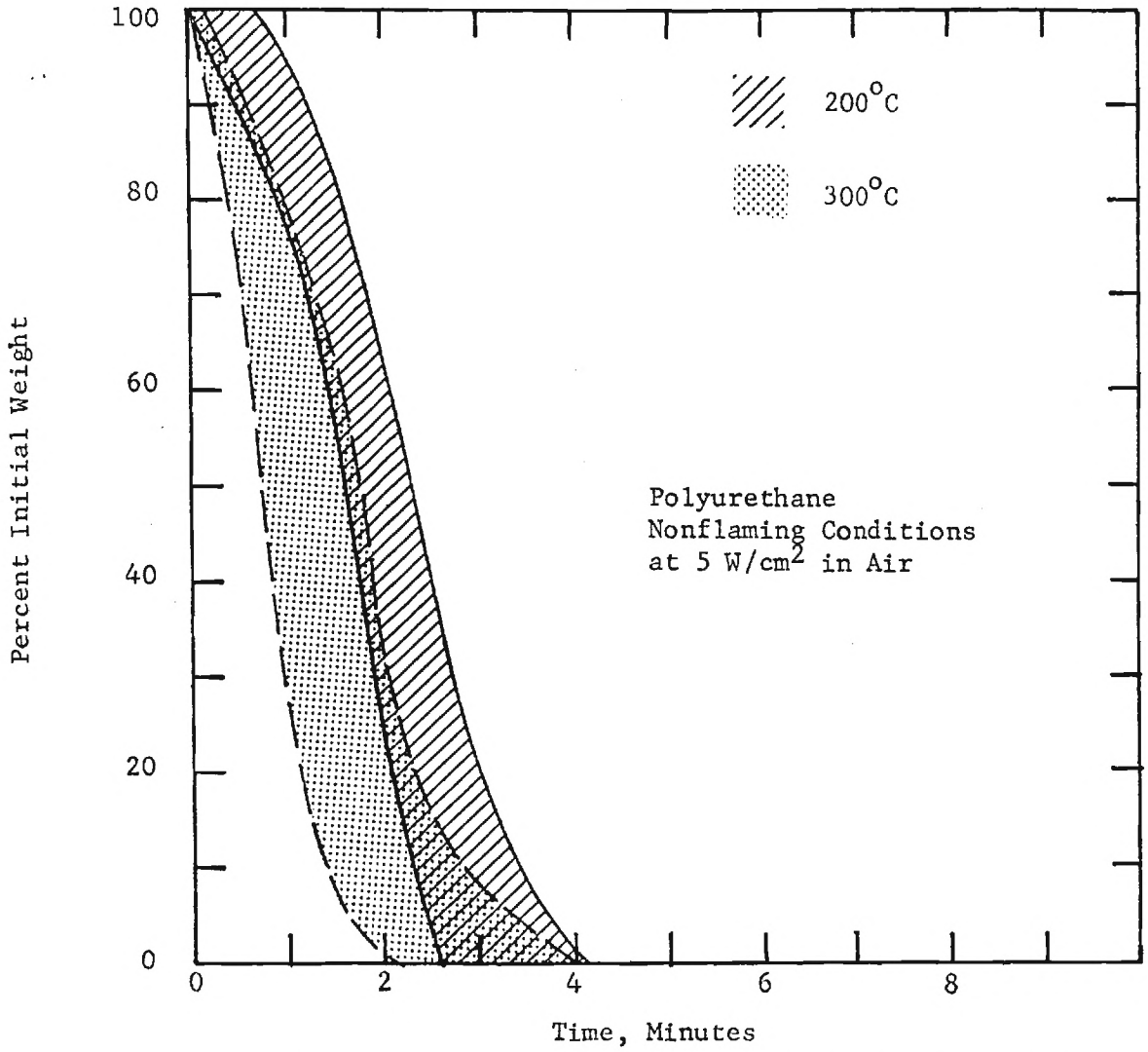


Figure 16. Comparison of Urethane Sample Weight Loss Behavior at 200°C and 300°C.

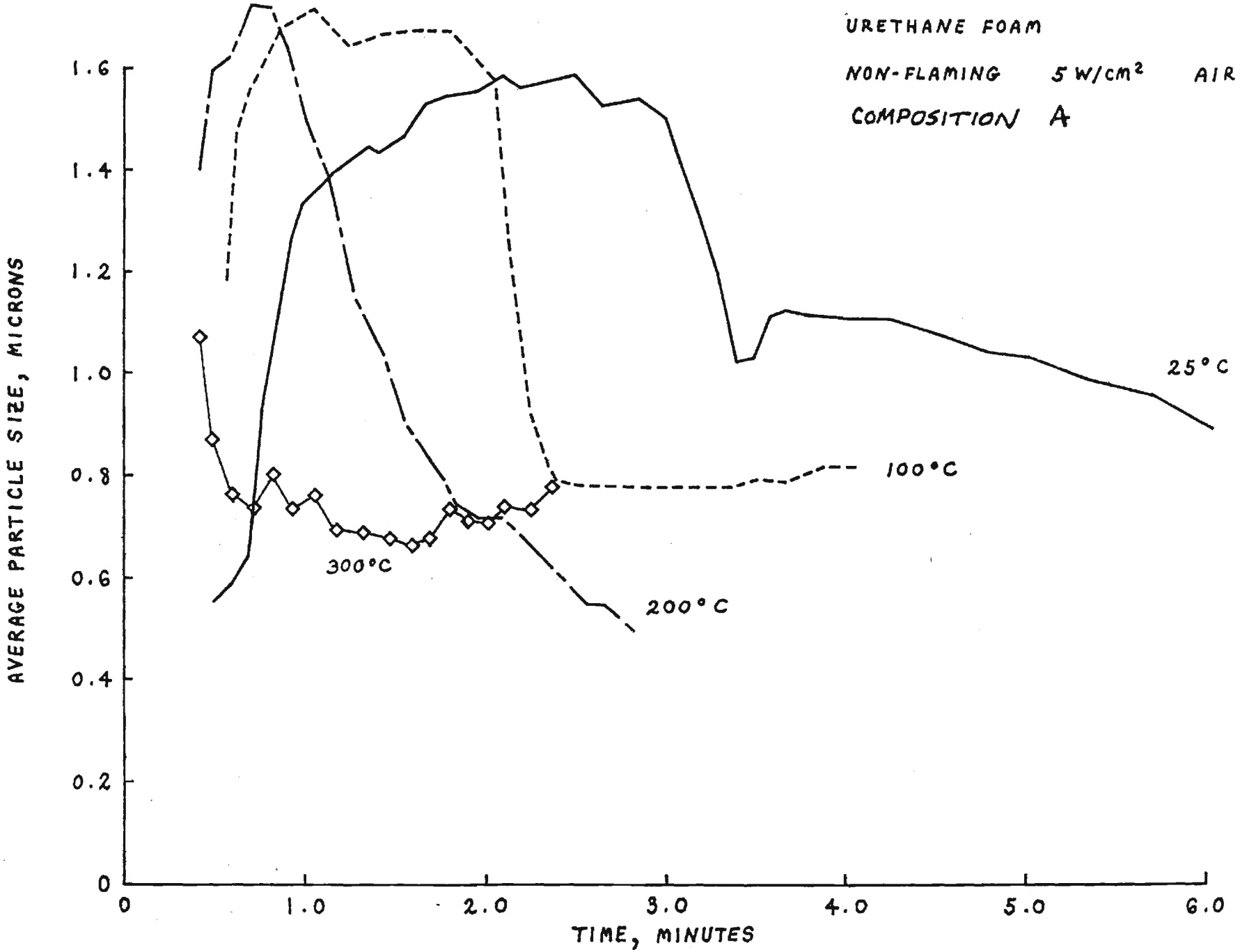


Figure 17. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane.

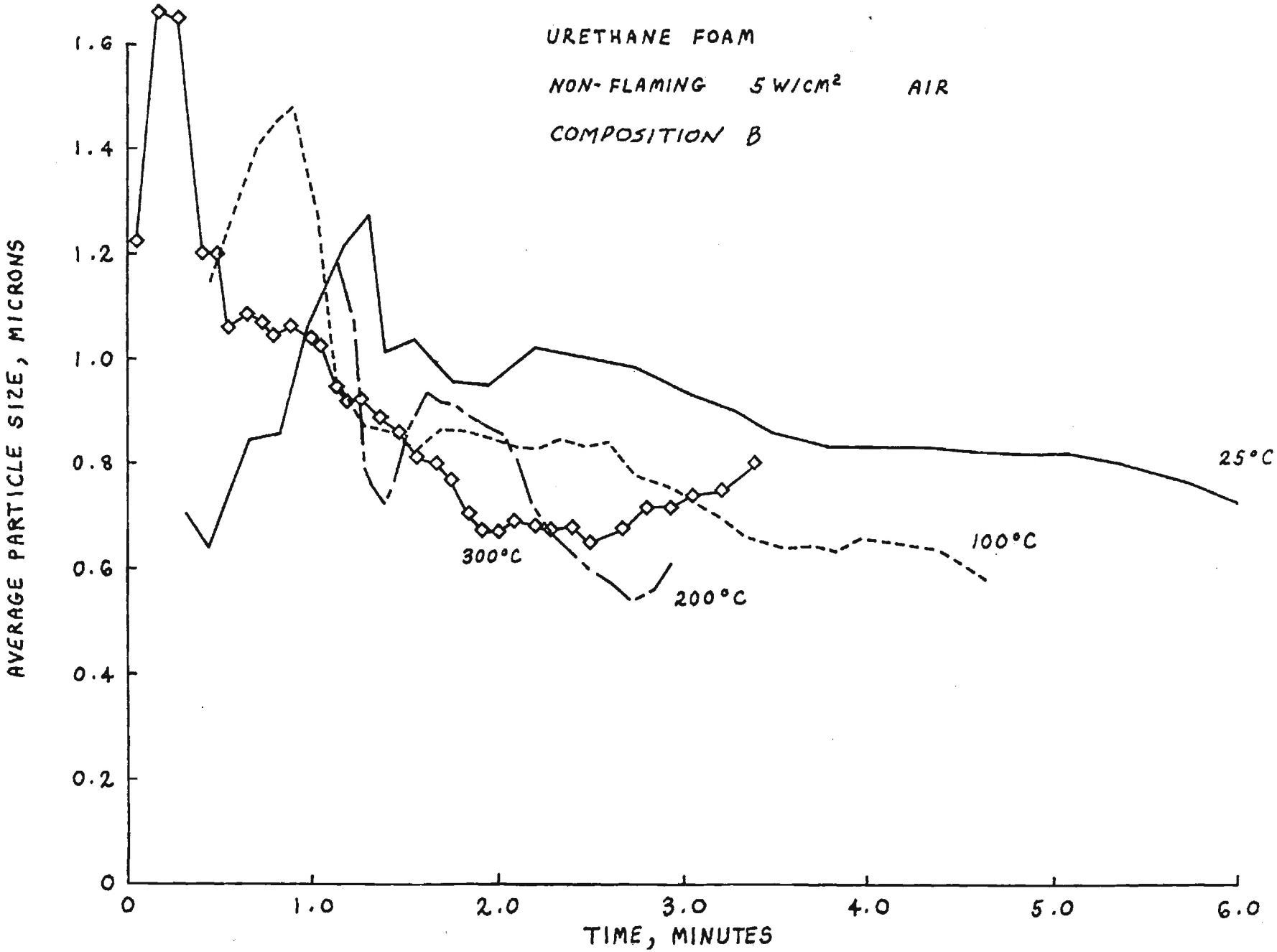


Figure 18. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

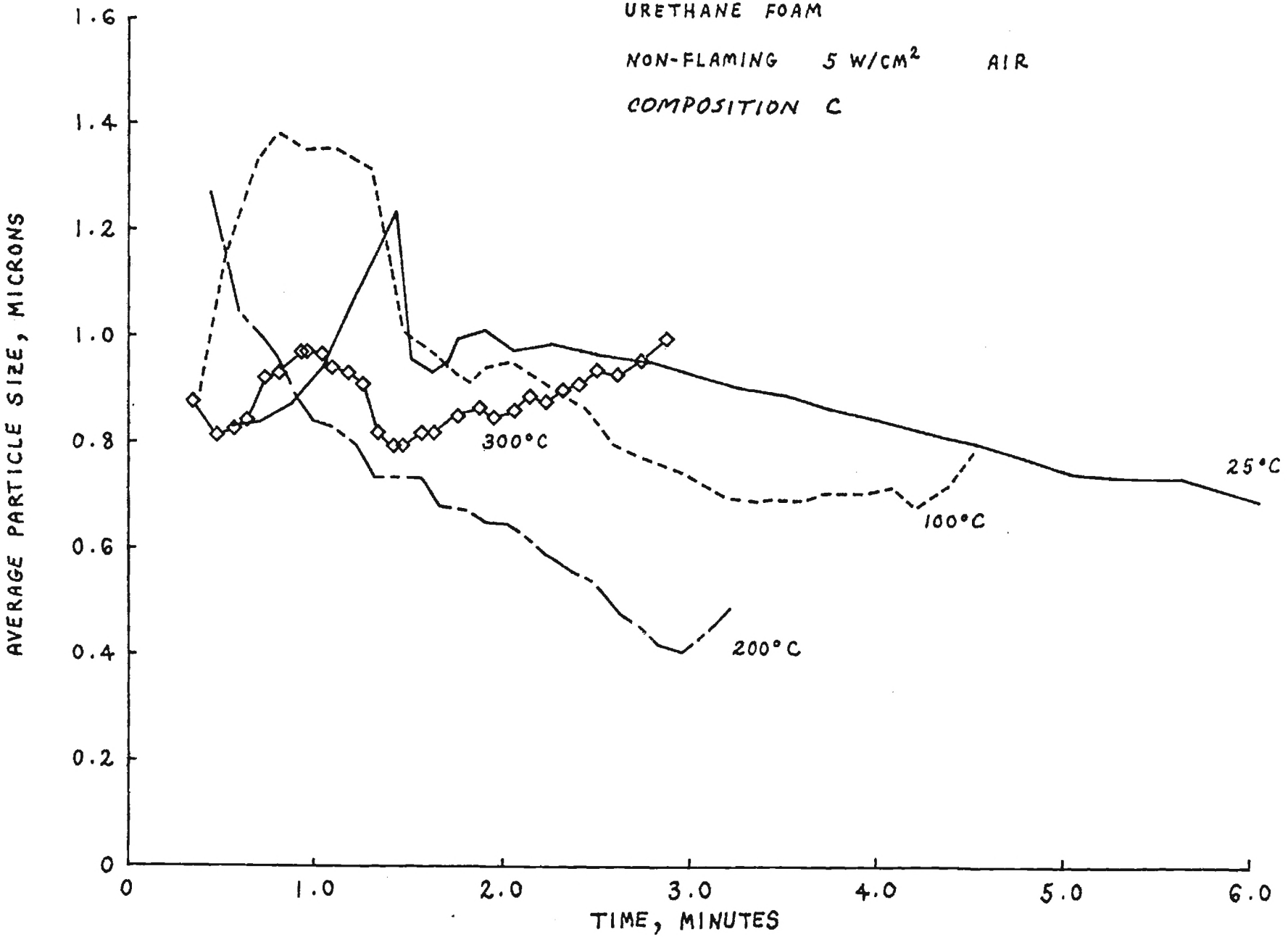


Figure 19. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

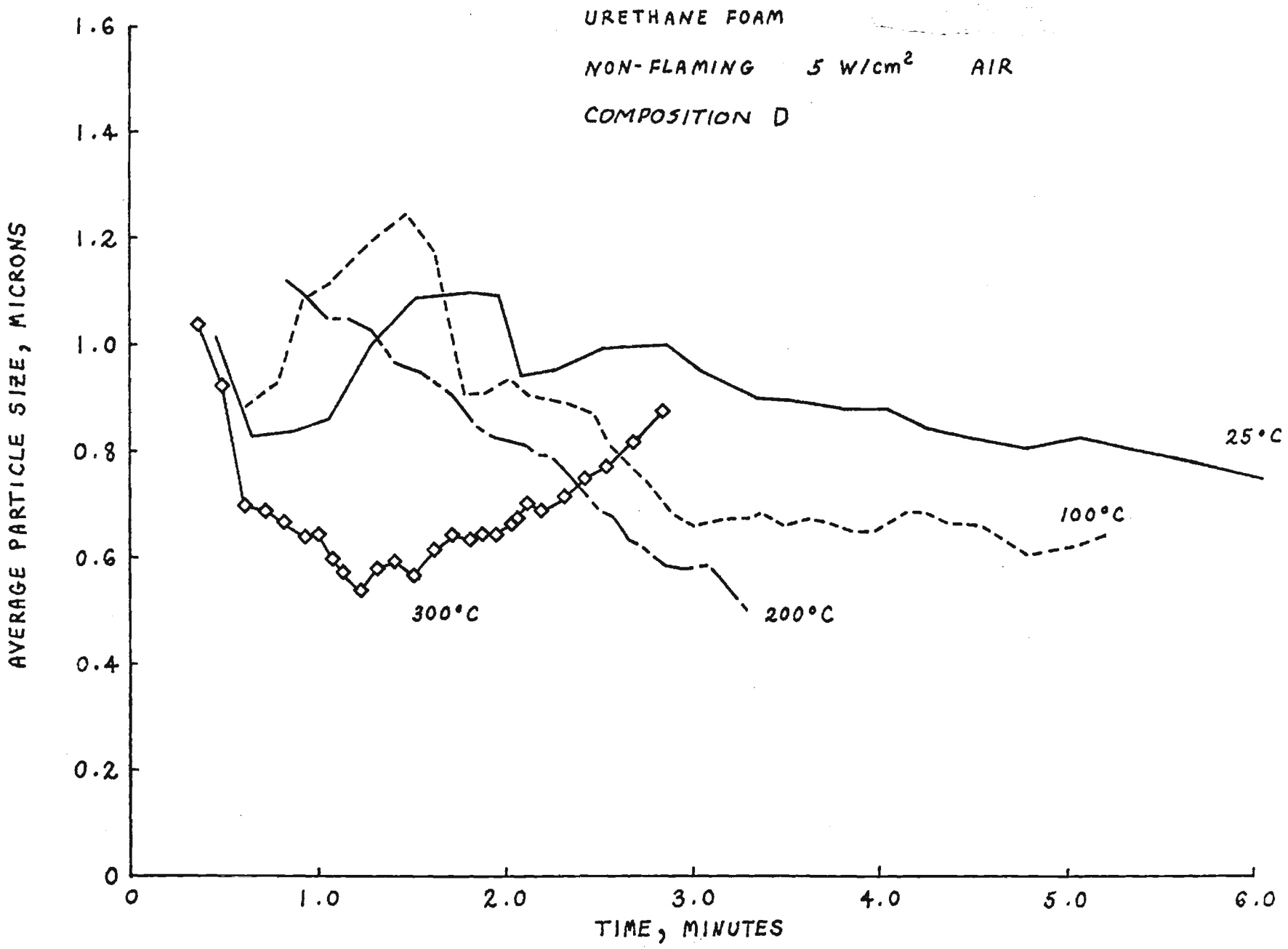


Figure 20. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Non-flaming Polyurethane

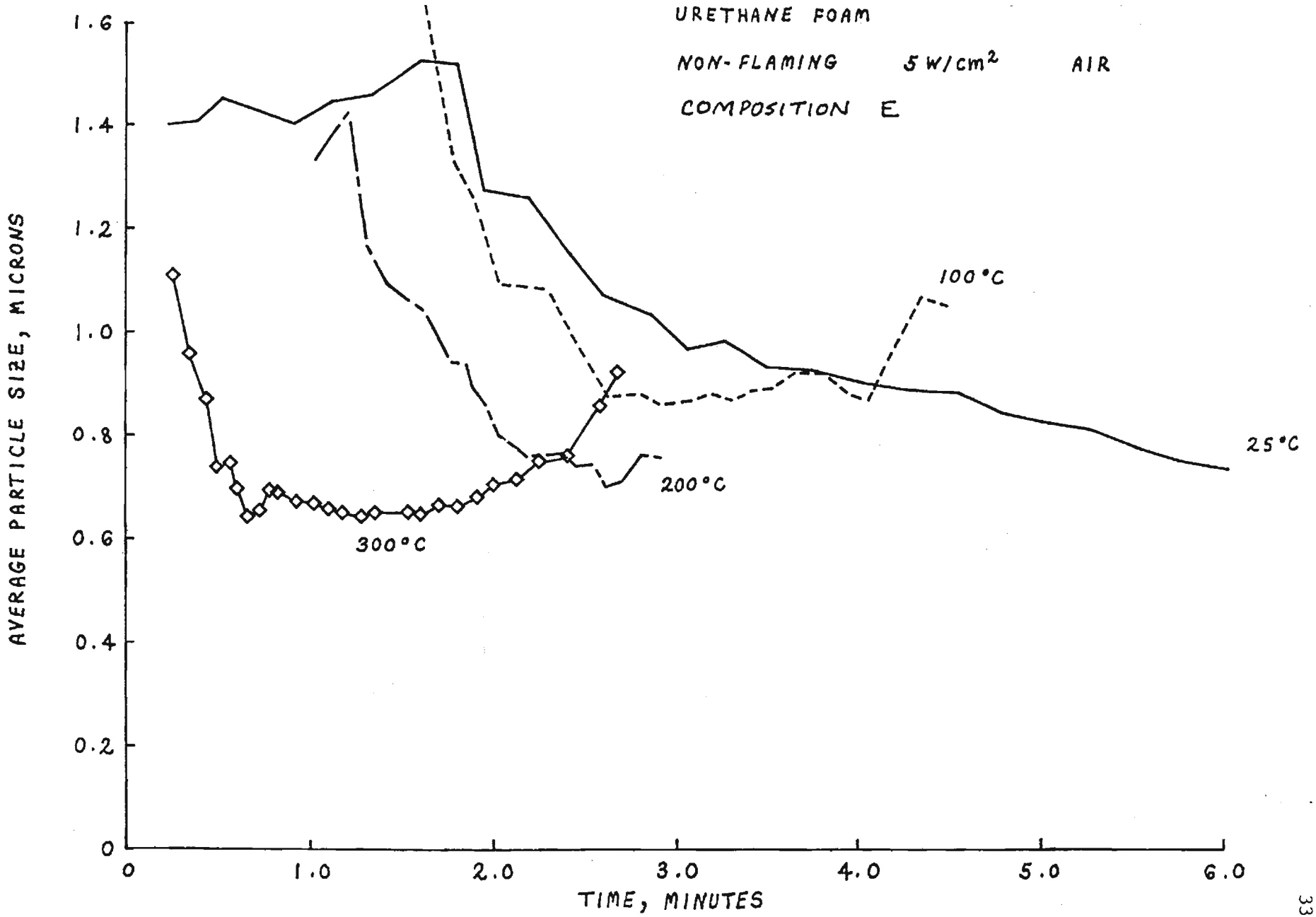


Figure 21. Time Resolved Smoke Particle Size Behavior under High Temperature Conditions - Nonflaming Polyurethane

Optical density behavior during high temperature tests are presented in Figures 22 through 26. Examination of these figures shows that, in general, increasing the environmental temperature results in a reduction in overall optical density levels, where the maximum optical densities are reduced considerably for each temperature increase. Of particular interest is the fact that optical density levels for all tests conducted at 300°C were negligble, and thus do not appear in Figures 22 through 26.

Summary

Nonflaming tests of flexible urethane foams in atmospheric temperatures up to 300°C provide data that show that the effect of increasing temperature is to increase the pyrolysis (and weight loss) rate of the samples. In general, mean particle size data indicate that after the maximum particle size is observed, smaller particles are generated as ventilation gas temperature increases. The data also show that compositions A and E produce larger particles than samples B, C and D for longer periods at each ventilation gas temperature except 300°C. Finally, maximum optical densities are considerably reduced as the environmental temperature is increased. These results indicate that the smoke particulates generated under nonflaming conditions are probably predominantly composed of condensible liquid pyrolysis products; since the nucleation and/or condensation processes would be considerably retarded at the higher temperatures.

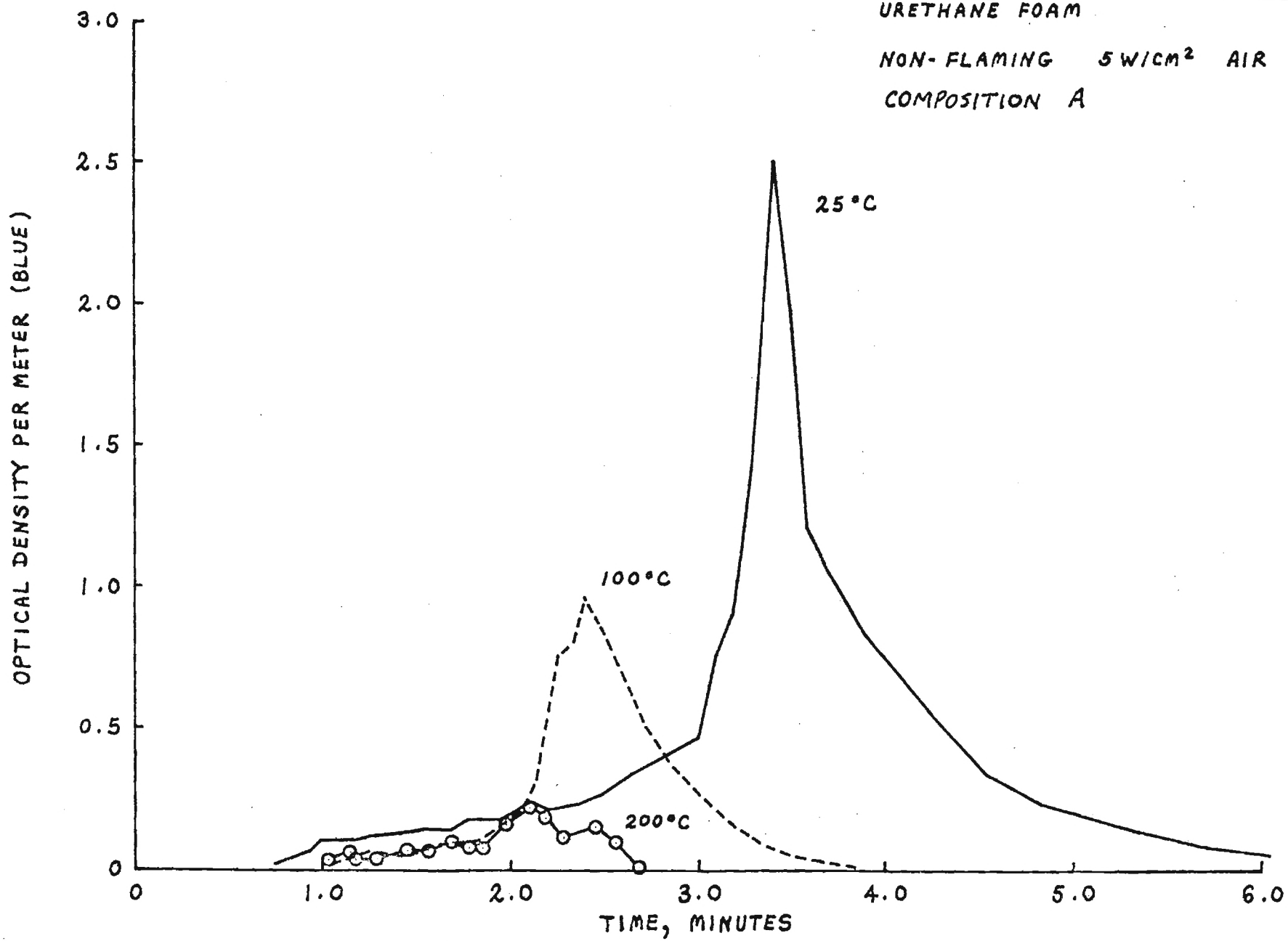


Figure 22. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane.

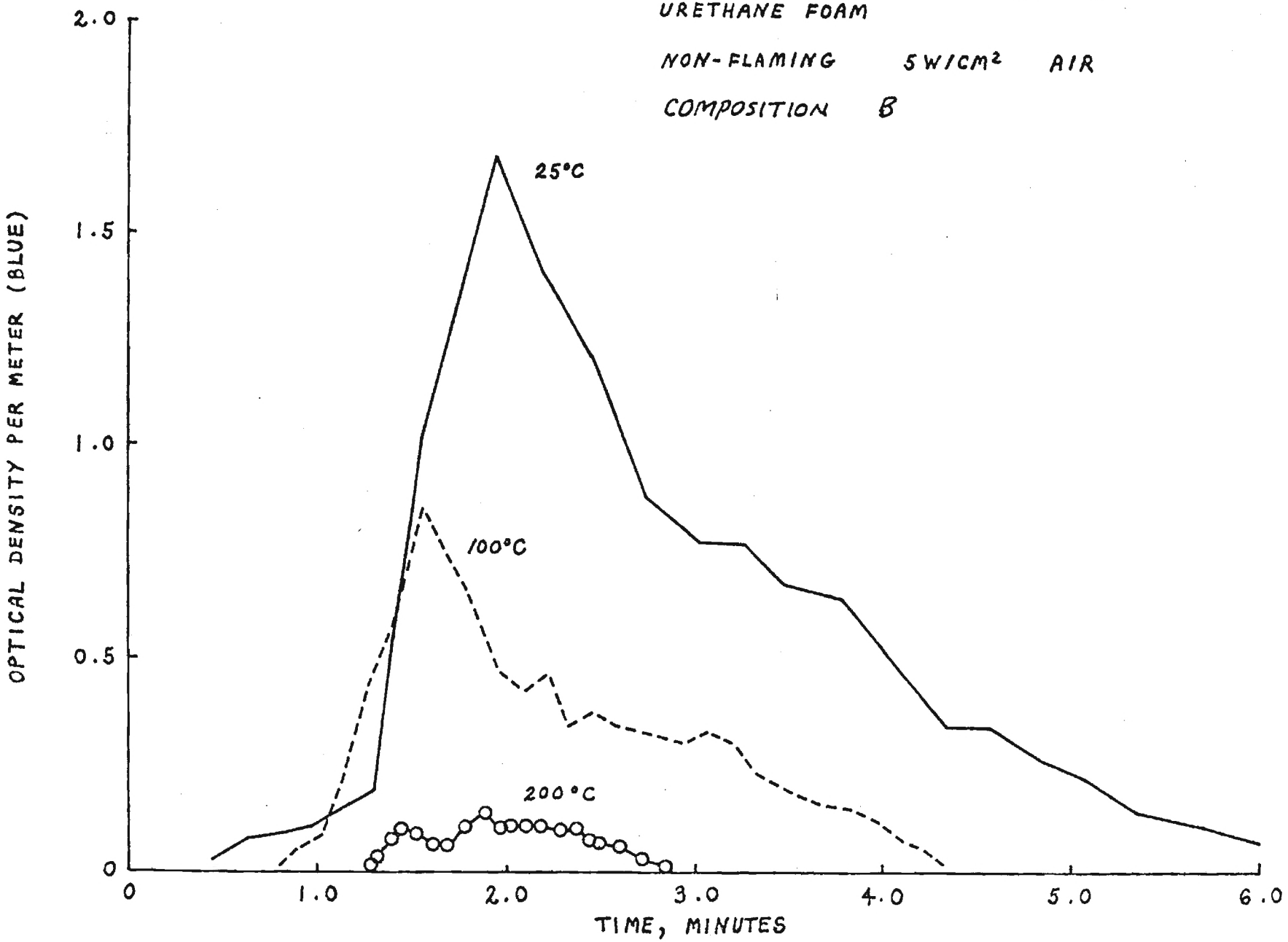


Figure 23. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane.

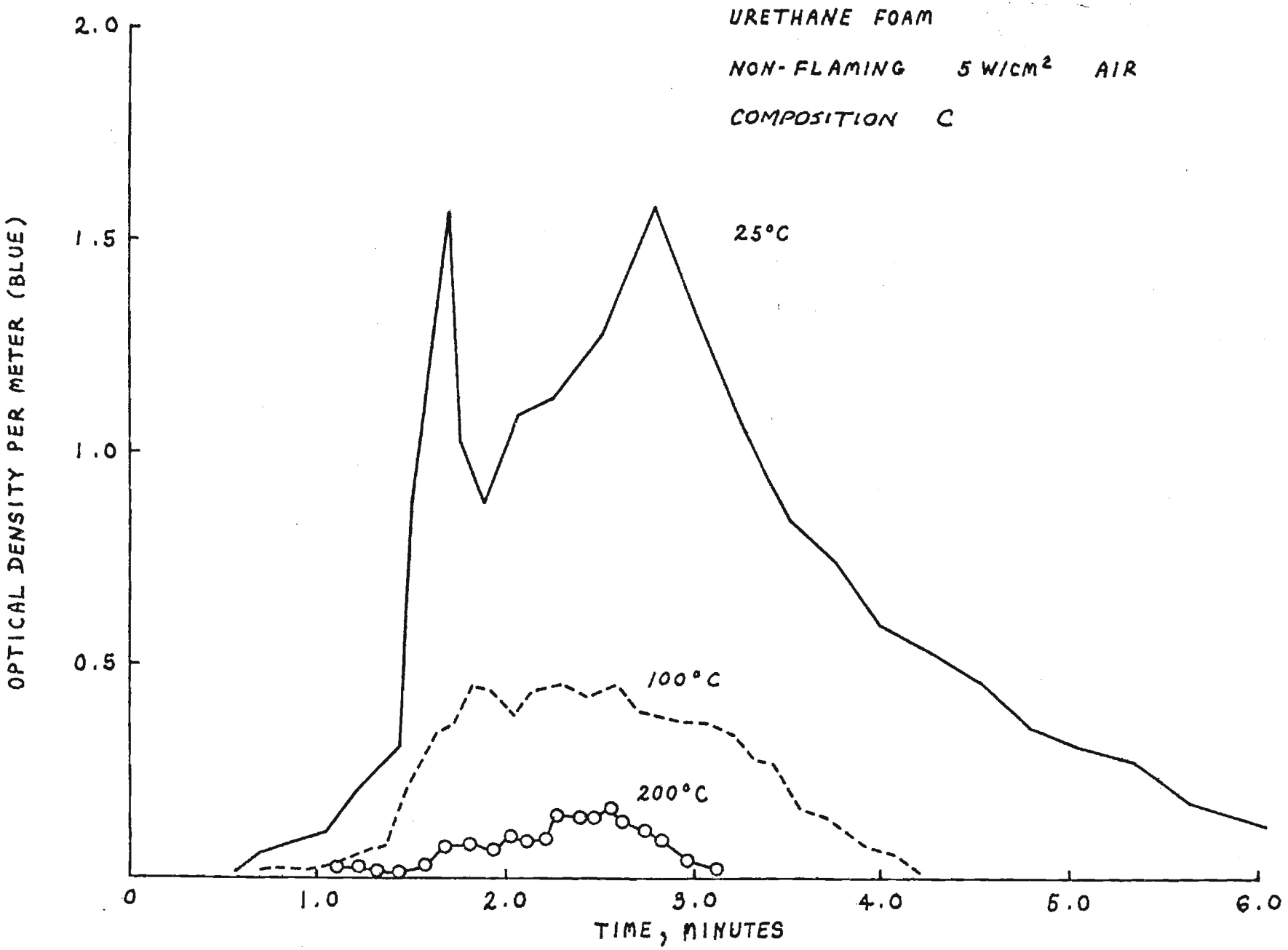


Figure 24. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

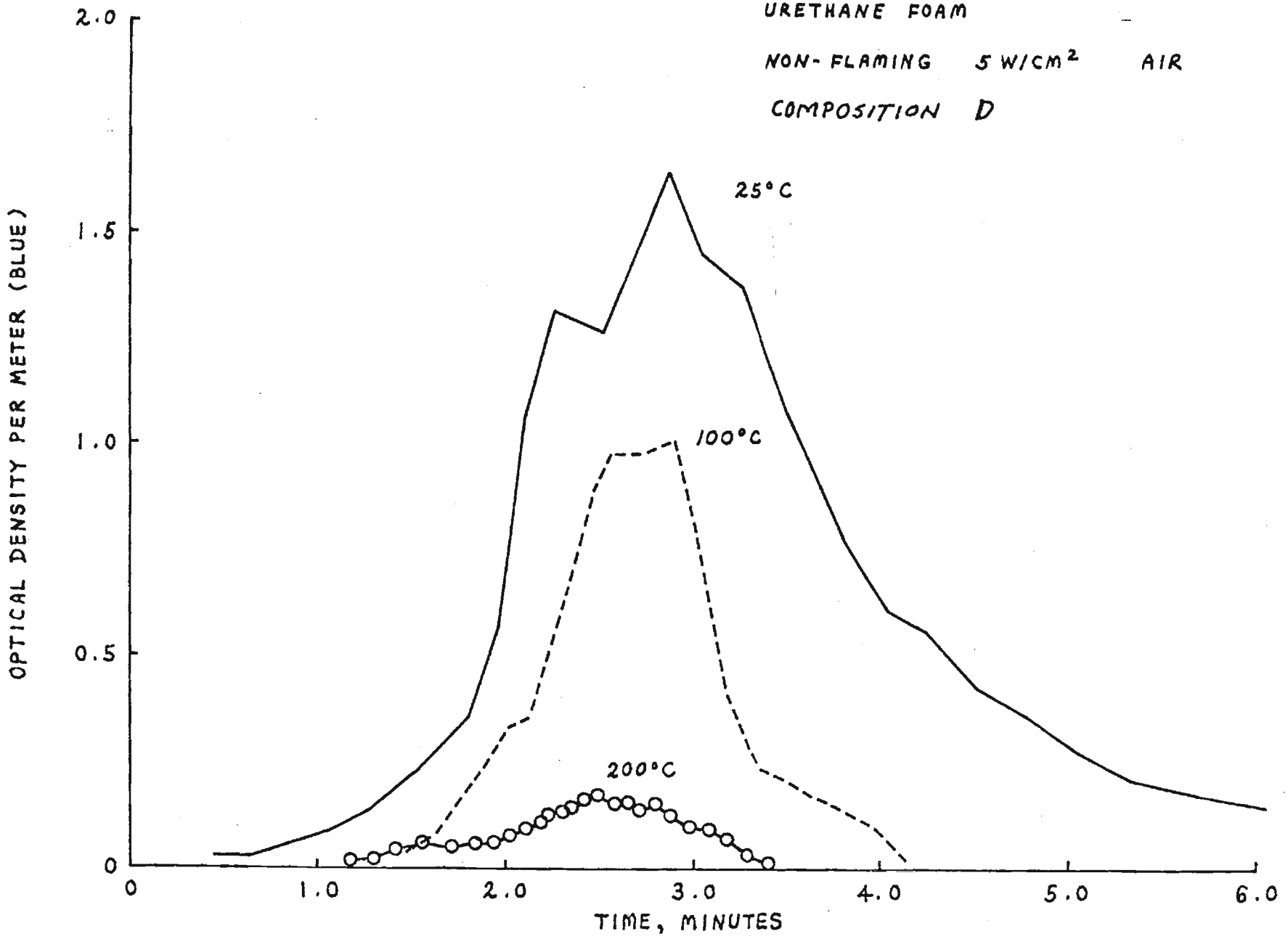


Figure 25. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

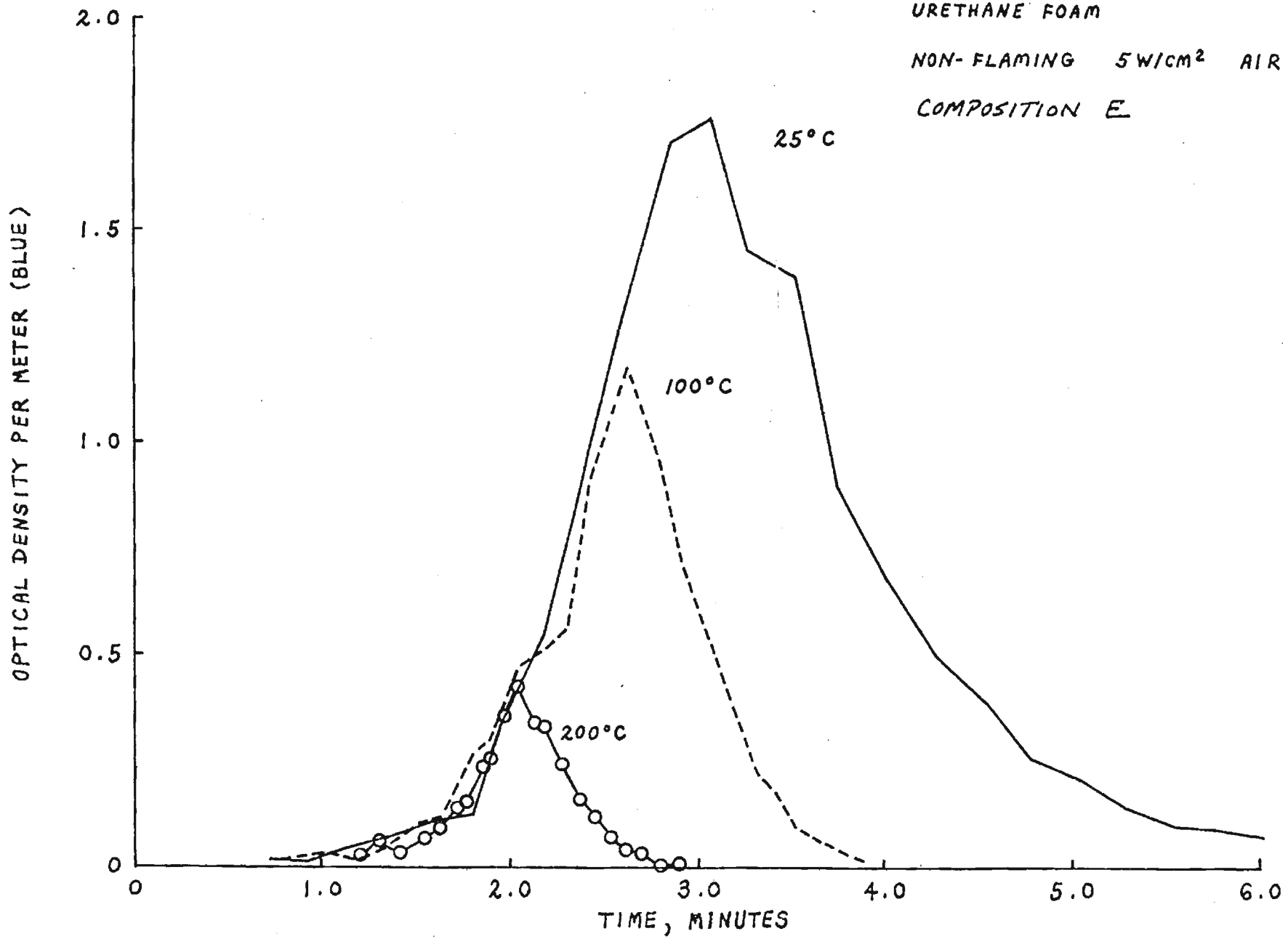


Figure 26. Smoke Optical Density Behavior under High Temperature Conditions - Nonflaming Polyurethane

V. RESULTS OF FLAMING TESTS OF FLEXIBLE URETHANES OF KNOWN COMPOSITION-PHYSICAL PROPERTIES DATA

Tests of the five flexible urethane samples under flaming conditions at ventilation gas (air) temperatures of 25°C, 100°C, 200°C and 300°C have been completed. Flaming ignition is initiated by a propane pilot burner while the sample is exposed to 5 W/cm^2 radiant flux. This series of tests has been limited to in situ optical system and force transducer measurements due to previously mentioned problems with sampling measurements at high temperatures and due to the nature of the smoke produced by flaming combustion in the room temperature (25°C) tests. In the flaming tests at 25°C, the mass of smoke particulates collected on the plates of the cascade impactor is too small to be accurately measured due to the fact that most of the particles are below the size range of the cascade impactor. Also, test conditions tend to change too rapidly to be measured with the Electrical Aerosol Analyzer, which requires a 1.5 minute scan for each determination of size distribution. Thus, no aerosol sampling system measurements will be presented for these low temperature, flaming tests.

Figures 27 and 28 show the weight loss data for the four ventilation gas temperatures which have been studied. The data are presented in characteristic bands for each temperature, where all samples fall within the indicated envelopes. These results show that the effect of increasing the environmental temperature is to increase the rate at which the sample is consumed under flaming conditions, although the effect of temperature is not as dramatic as in the nonflaming results. Also, the addition of the fire retardants has not appreciably reduced the burning rate for the conditions tested.

Figures 29 through 33 describe the time dependence of the smoke particle mean diameter, D_{32}, measured for flaming urethane samples at the four ventilation gas temperatures. Note that the tests were begun at t = 2 minutes in all

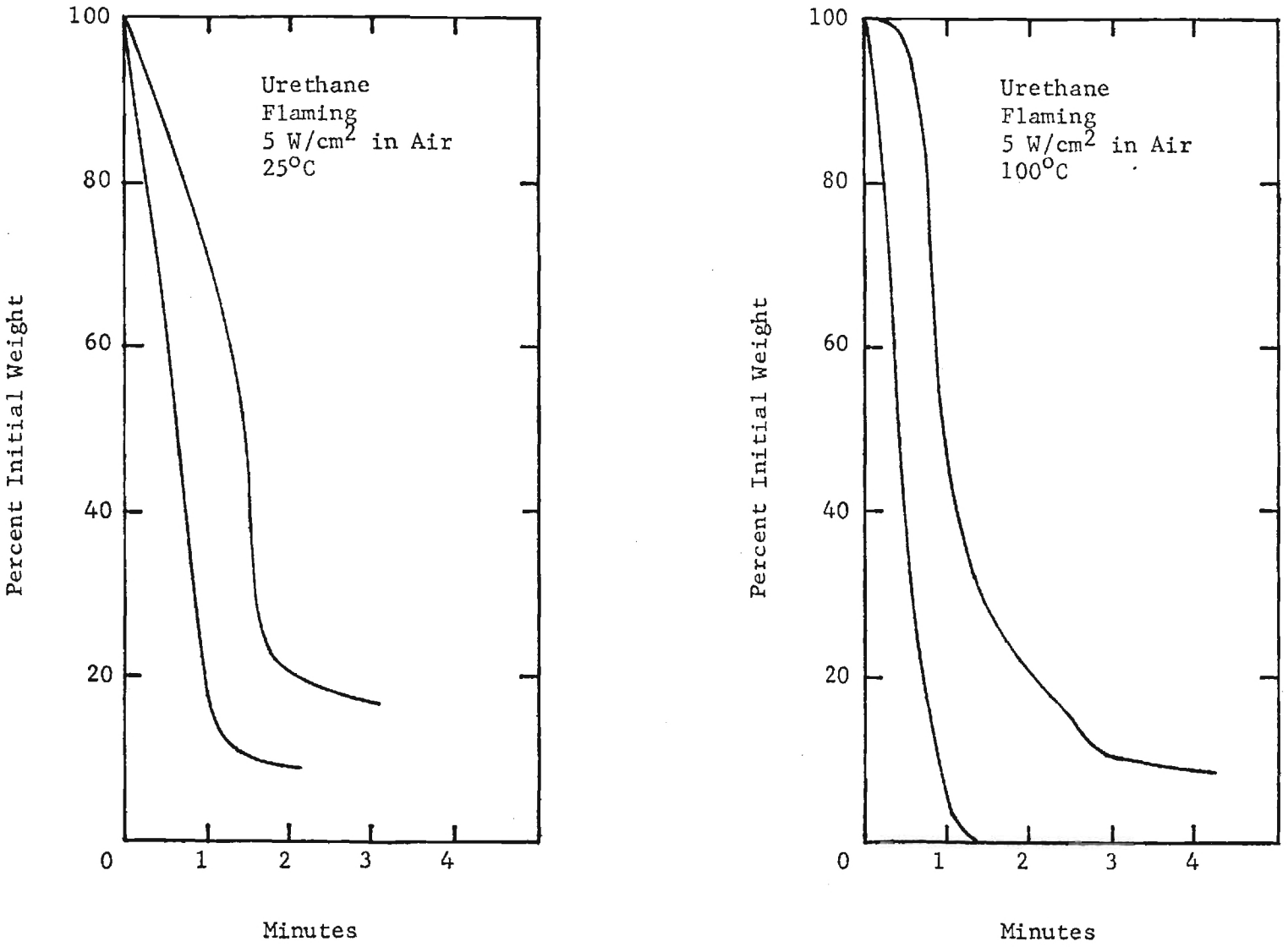


Figure 27. Urethane Sample Weight Loss Behavior at 100°C and Room Temperature - Flaming Conditions

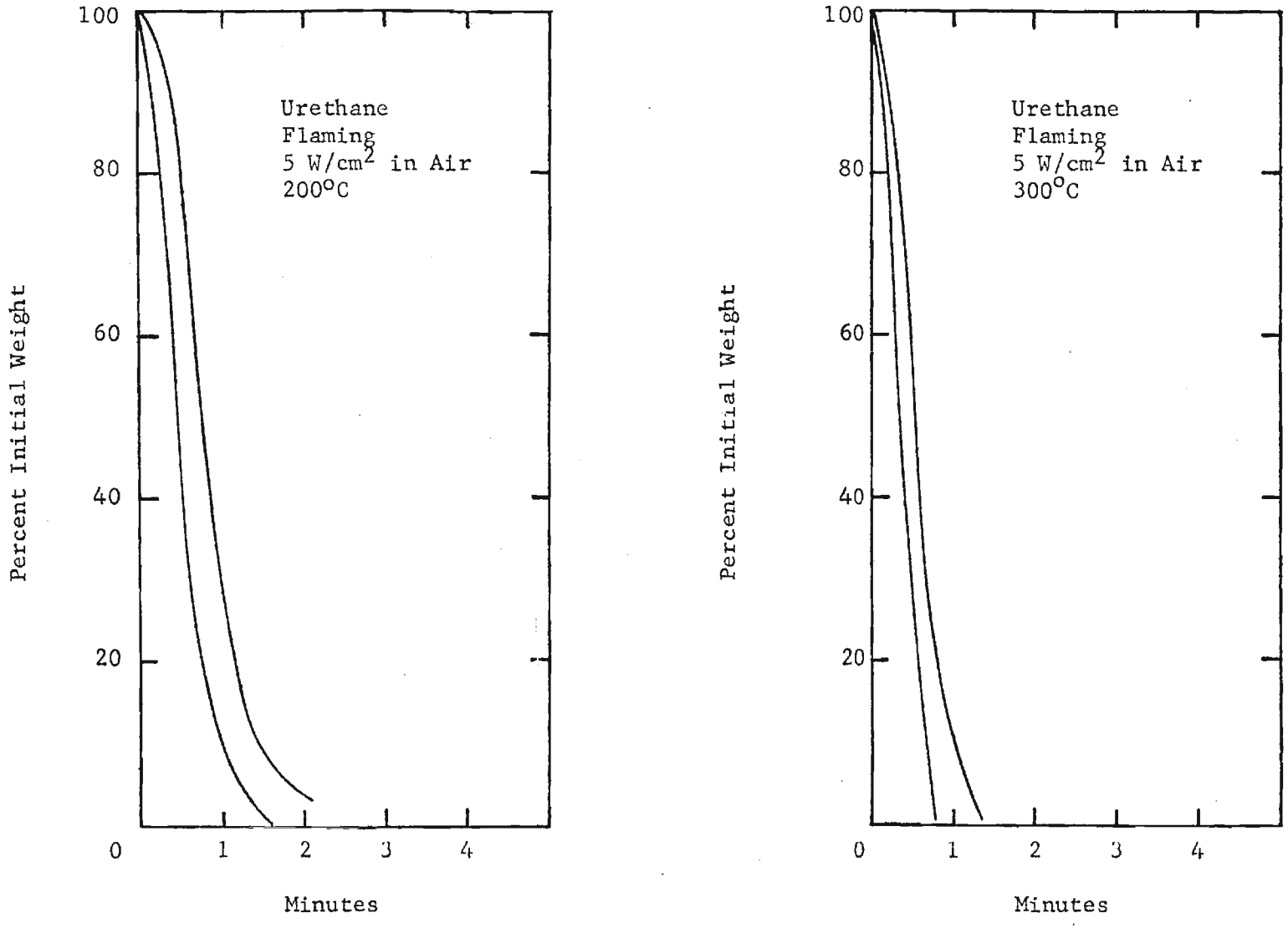


Figure 28. Urethane Sample Weight Loss Behavior at 200°C and 300°C - Flaming Conditions

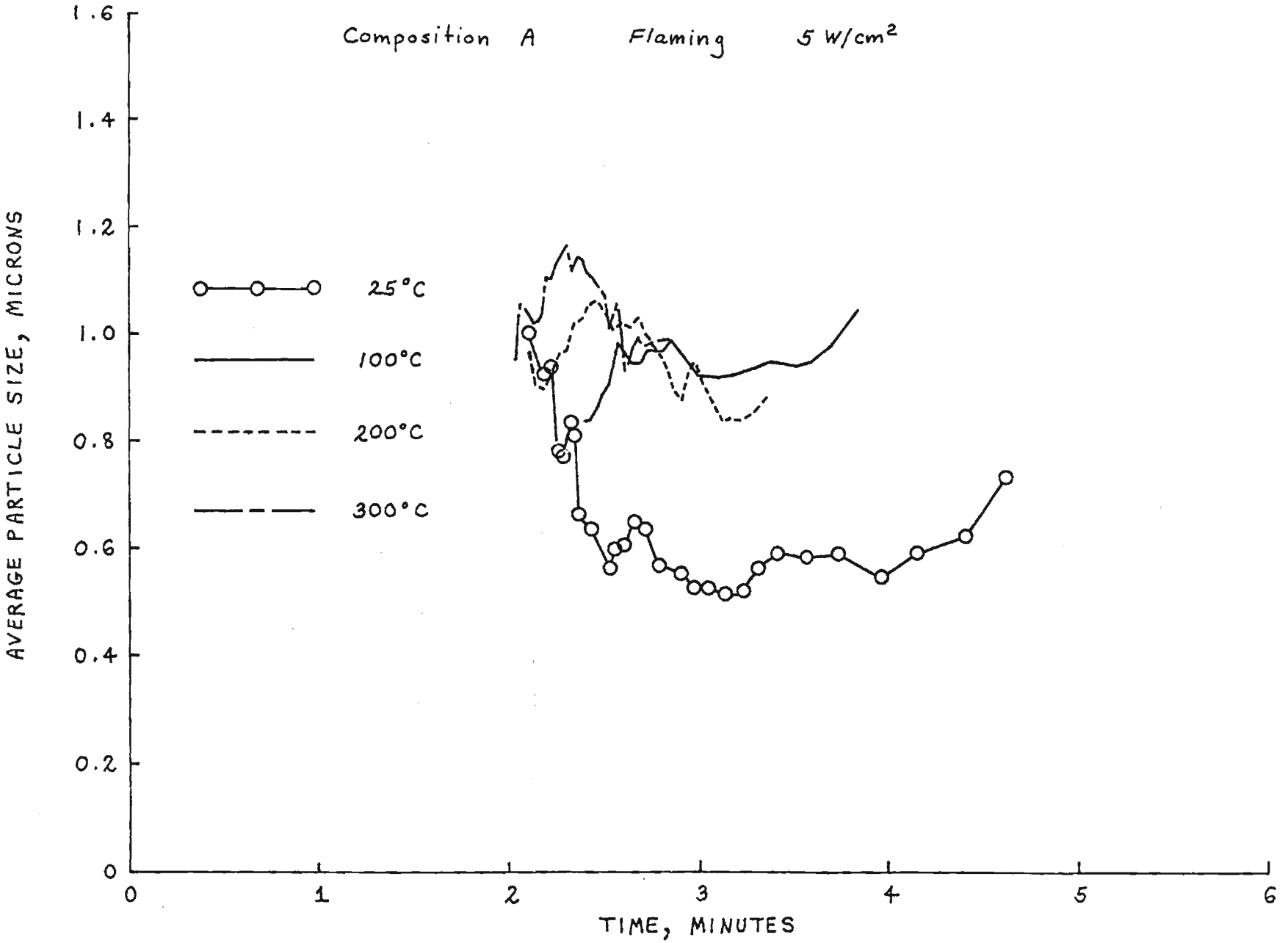


Figure 29. Time Resolved Smoke Particle Size Behavior under Different Temperature Conditions - Flaming Polyurethane

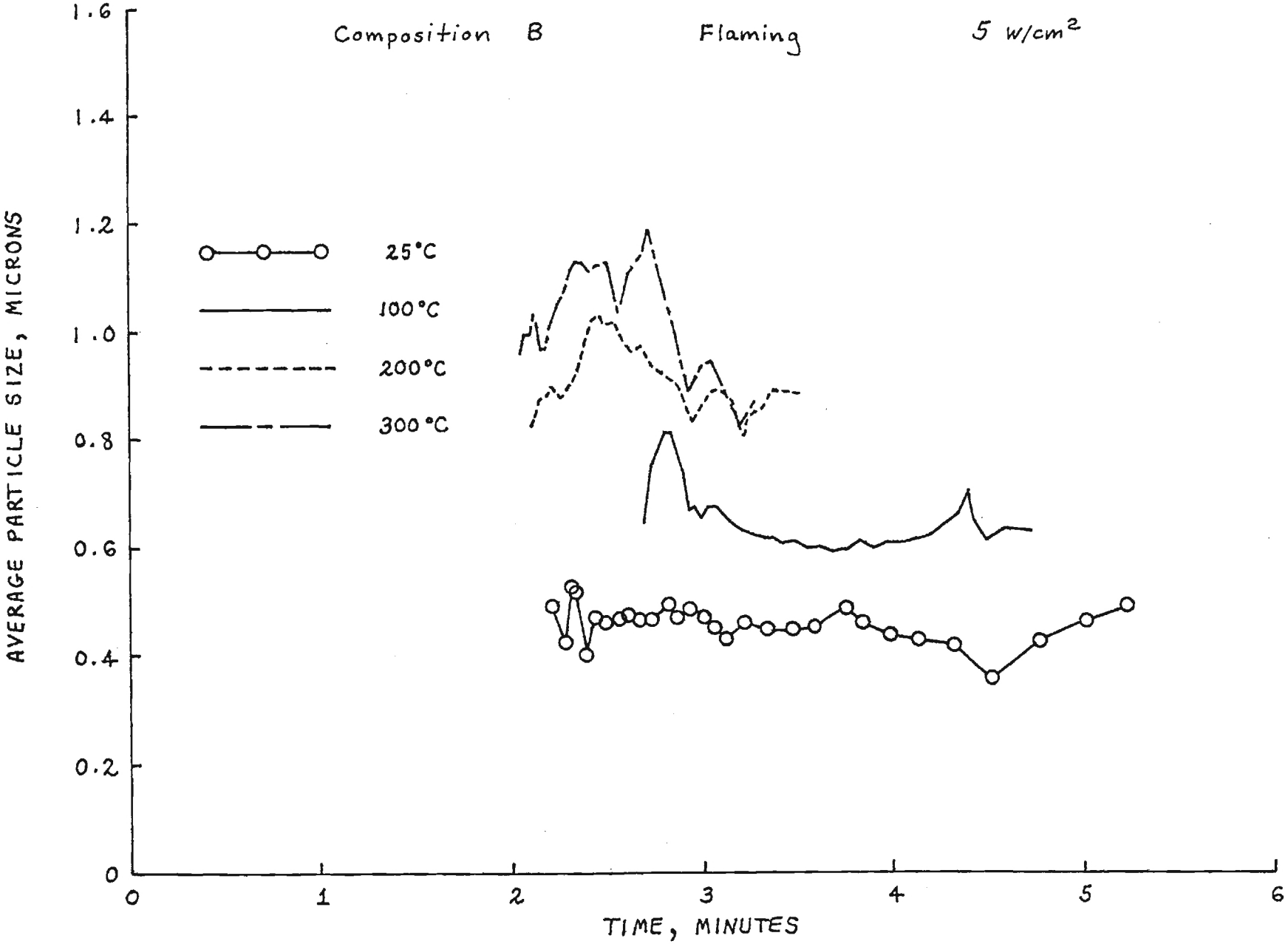


Figure 30. Time Resolved Smoke Particle Size Behavior under Different Temperature Conditions - Flaming Polyurethane

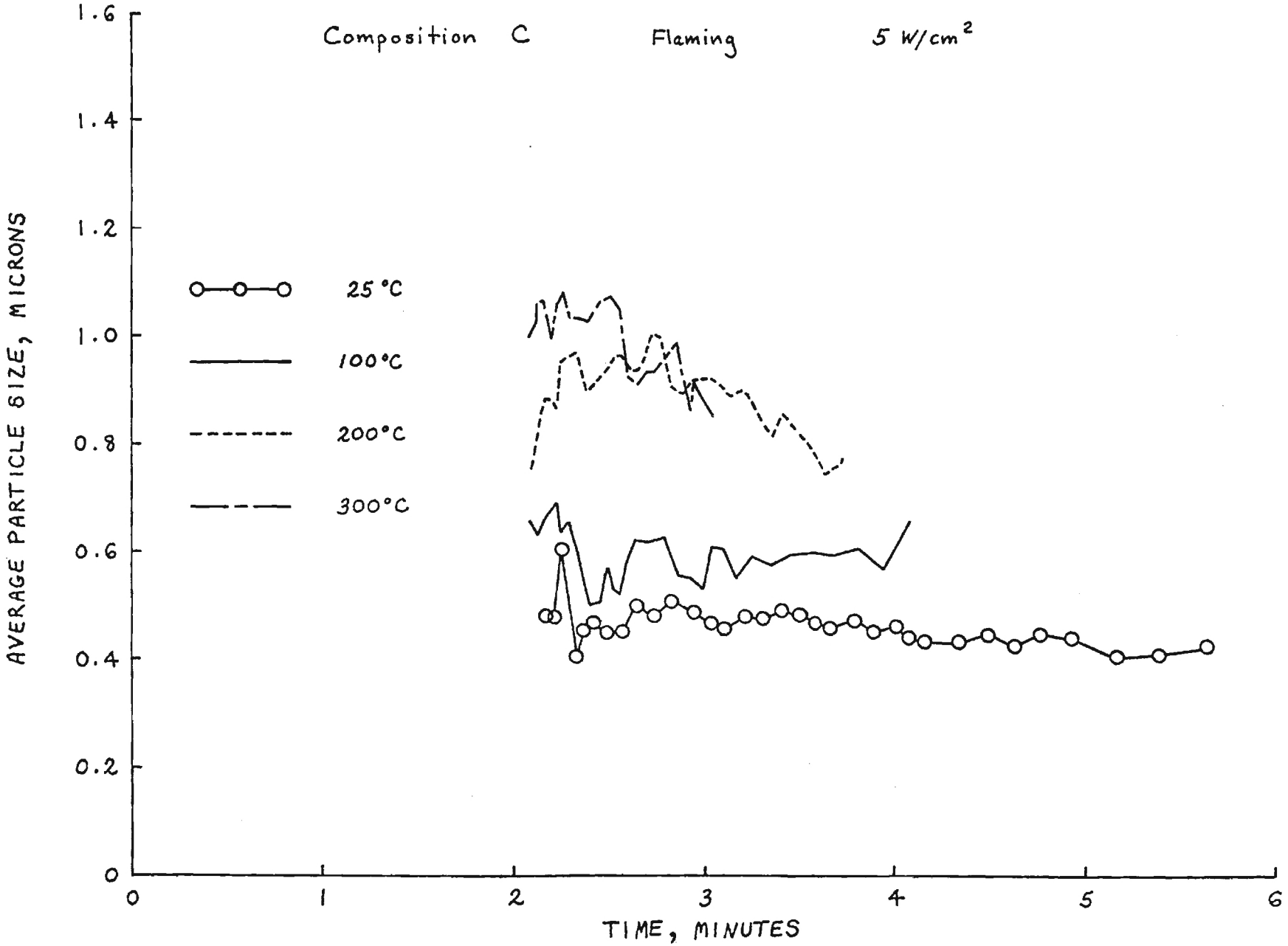


Figure 31. Time Resolved Smoke Particle Size Behavior under Different Temperature Conditions - Flaming Polyurethane

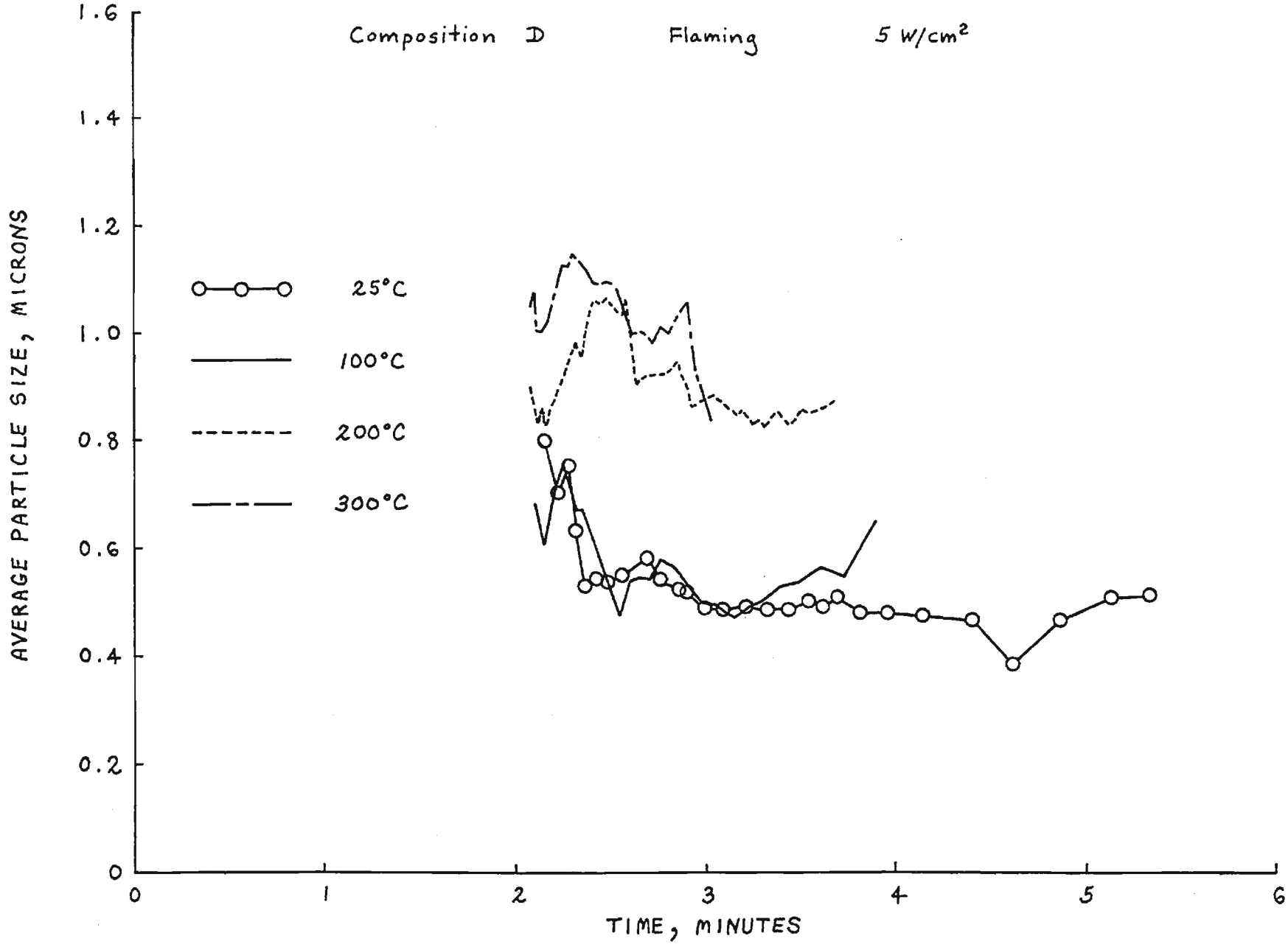


Figure 32. Time Resolved Smoke Particle Size Behavior under Different Temperature Conditions - Flaming Polyurethane

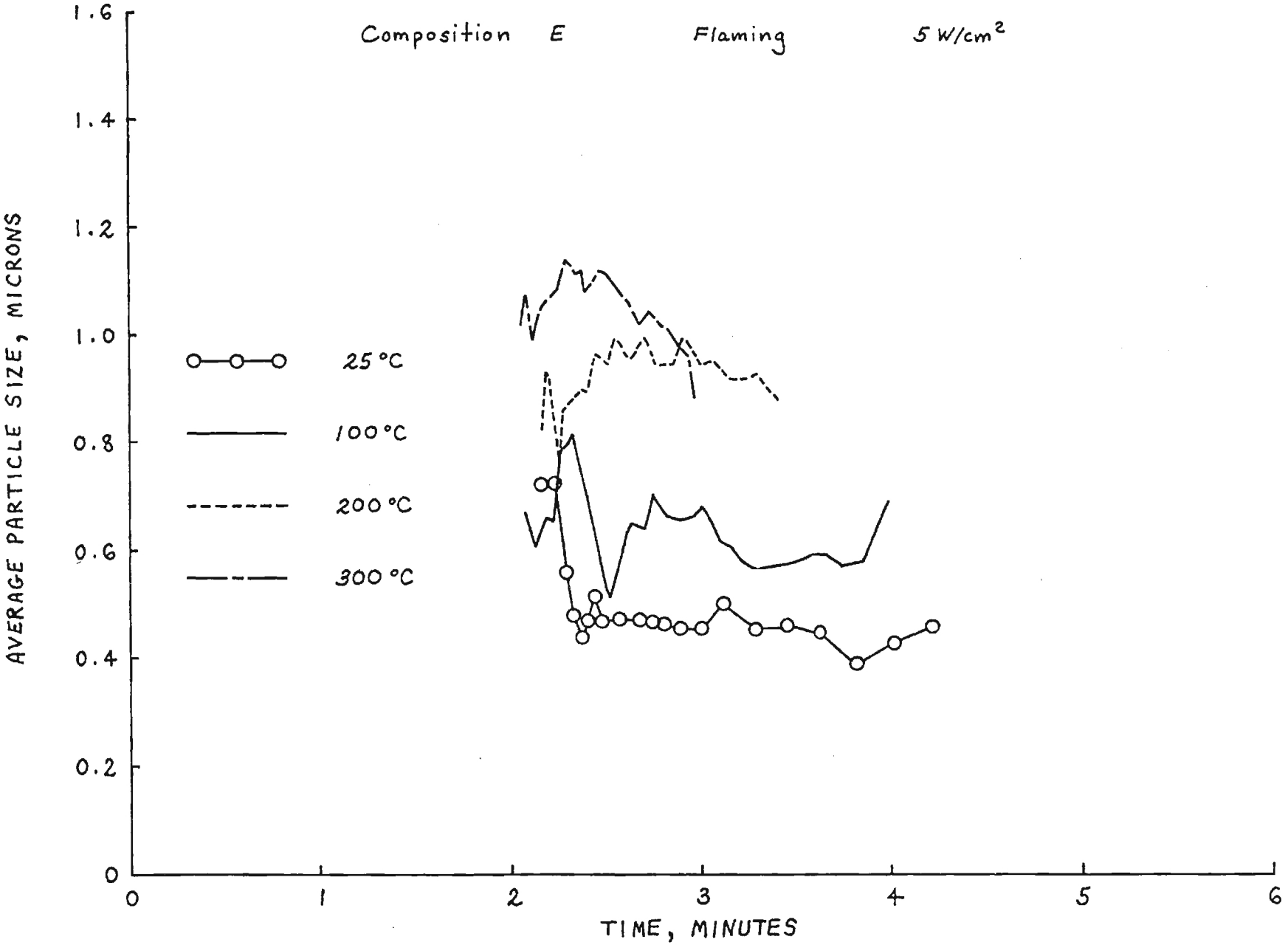


Figure 33. Time Resolved Smoke Particle Size Behavior under Different Temperature Conditions - Flaming Polyurethane

cases presented. The data indicates that in general, larger particles are generated as the environmental temperature is increased. In addition, the results show that there is very little difference in measured particle sizes among the five compositions. An exception is noted in the case of composition A, where particle sizes tend to be larger than those generated by the other samples in the room temperature tests.

Measurements of the time evolution of the optical density for flaming urethane smokes are presented in Figures 34 through 38. Of particular interest in this data is the fact that in room temperature tests, the non-fire-retarded sample (composition A) generated considerably lower optical density levels than the other four fire-retarded samples. However, upon increasing the ventilation gas temperature to 100°C, the optical density levels of the fire-retarded samples were reduced to near the same levels as those observed for composition A. As the temperature increases from 100°C, the general tendency for all the samples is for the maximum optical densities to gradually increase.

Comparisons of the results of flaming tests with the results of non-flaming tests show that at room temperature, particle sizes at the time of maximum smoke production, are smaller under flaming conditions. At the highest ventilation gas temperature (300°C) however, particle sizes are greatest for flaming conditions. Maximum optical densities in nonflaming and flaming tests at room temperature are nearly the same for the fire-retarded samples (B,C,D and E); however, the maximum optical density for Sample A is considerably less in the flaming case than in the nonflaming case. As the environmental temperature increases, optical densities become greatest under flaming conditions for all five samples.

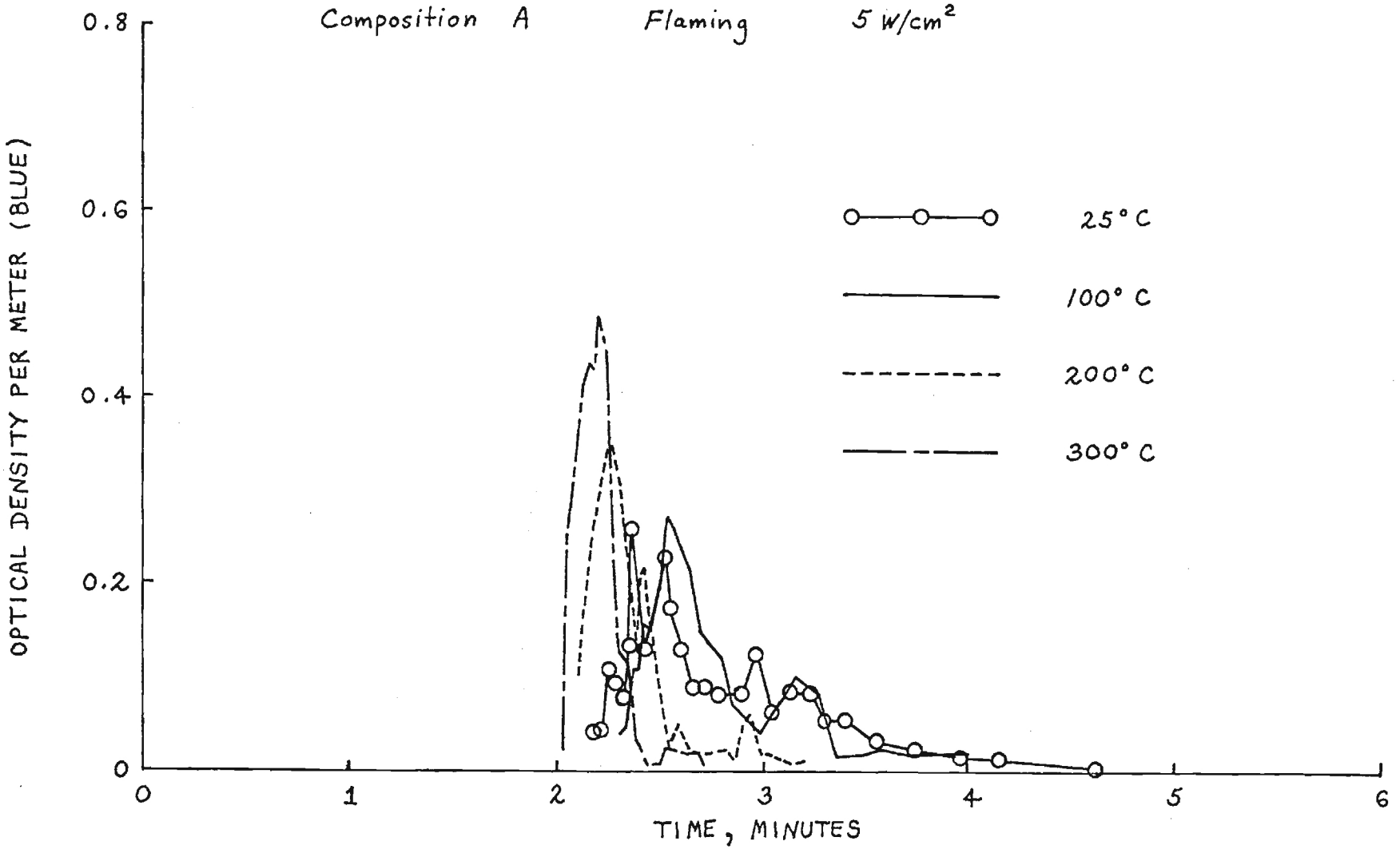


Figure 34. Smoke Optical Density Behavior under Different Temperature Conditions - Flaming Polyurethane

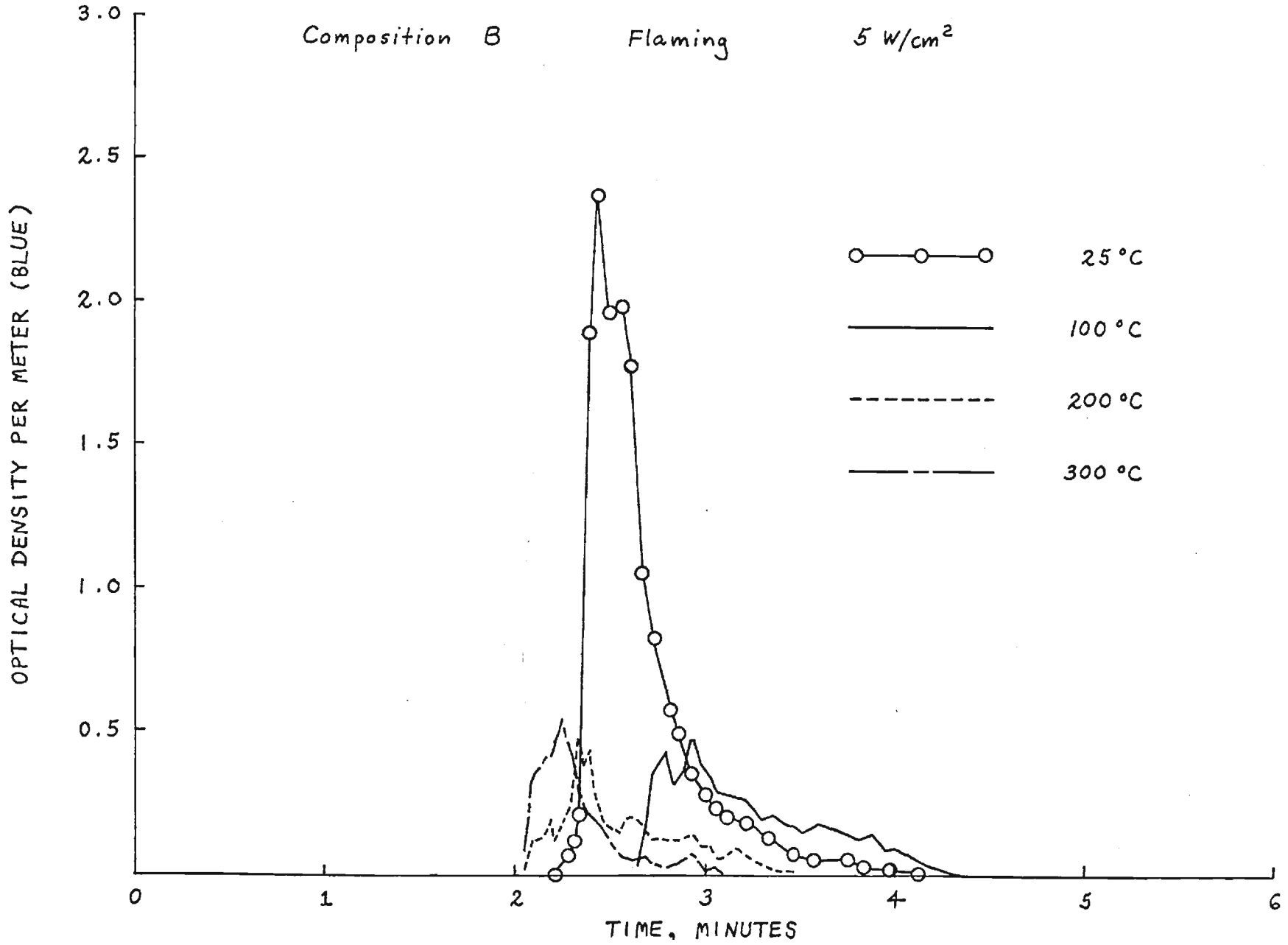


Figure 35. Smoke Optical Density Behavior under Different Temperature Conditions - Flaming Polyurethane

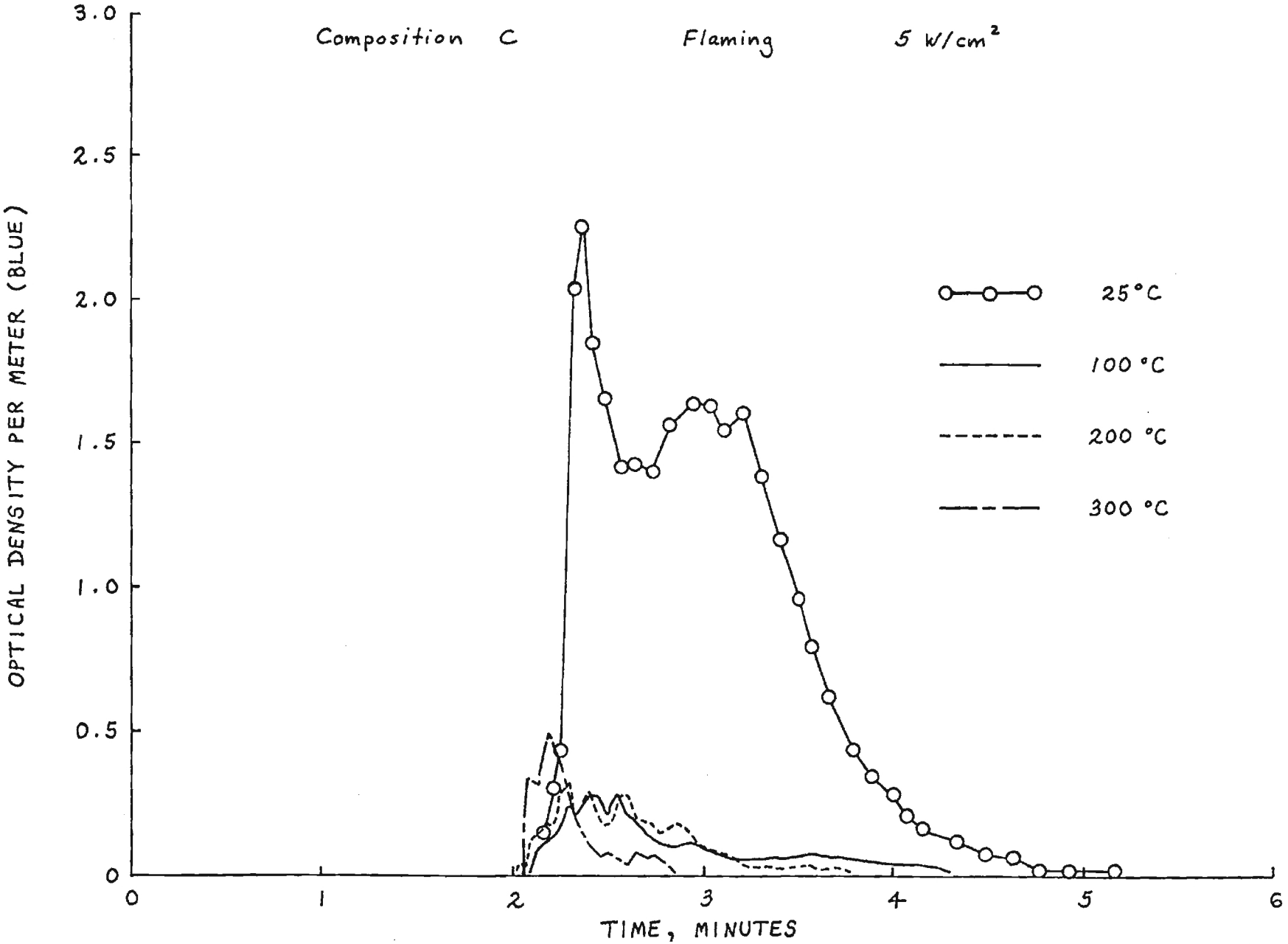


Figure 36. Smoke Optical Density Behavior under Different Temperature Conditions - Flaming Polyurethane

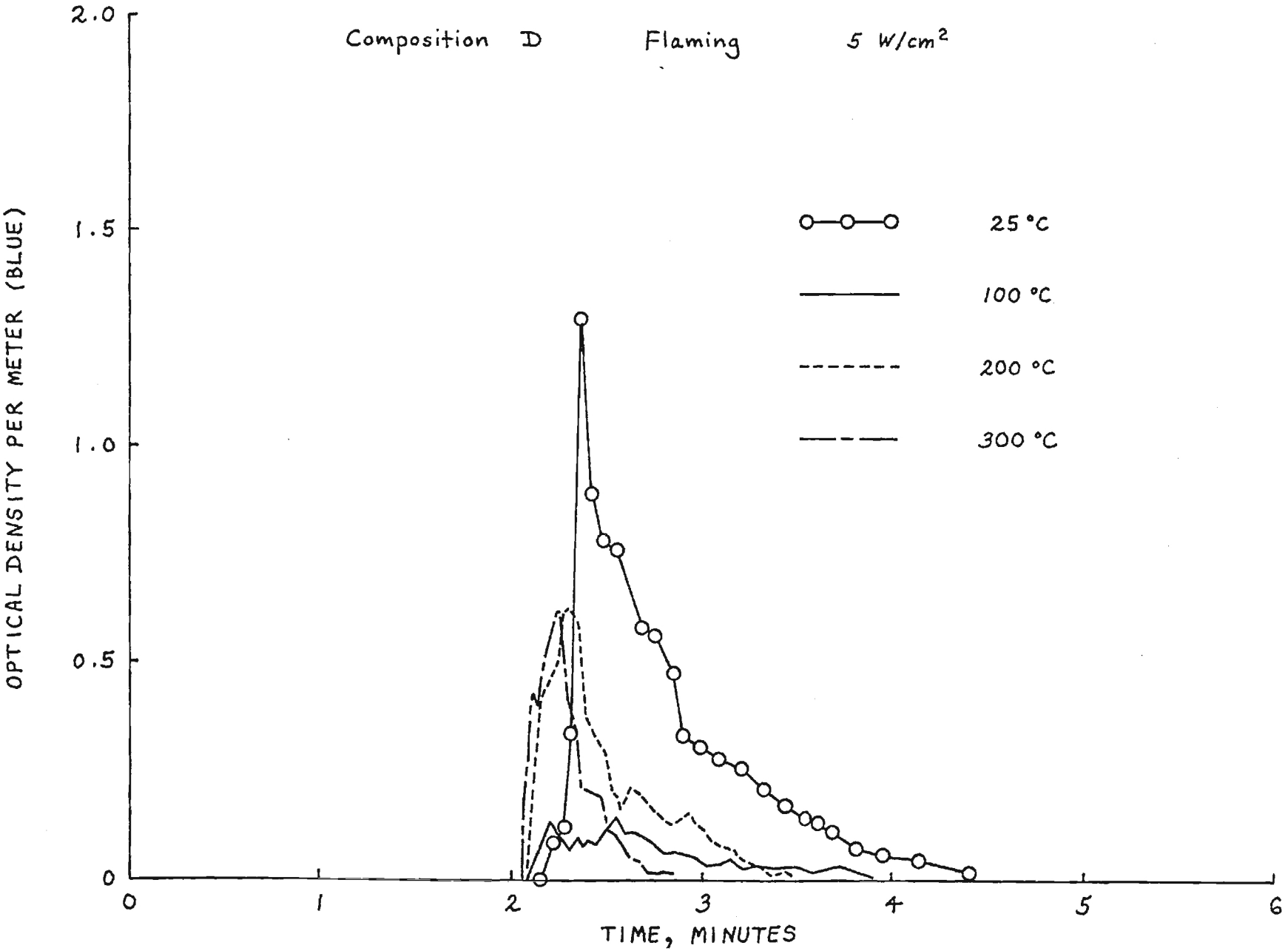


Figure 37. Smoke Optical Density Behavior under Different Temperature Conditions - Flaming Polyurethane

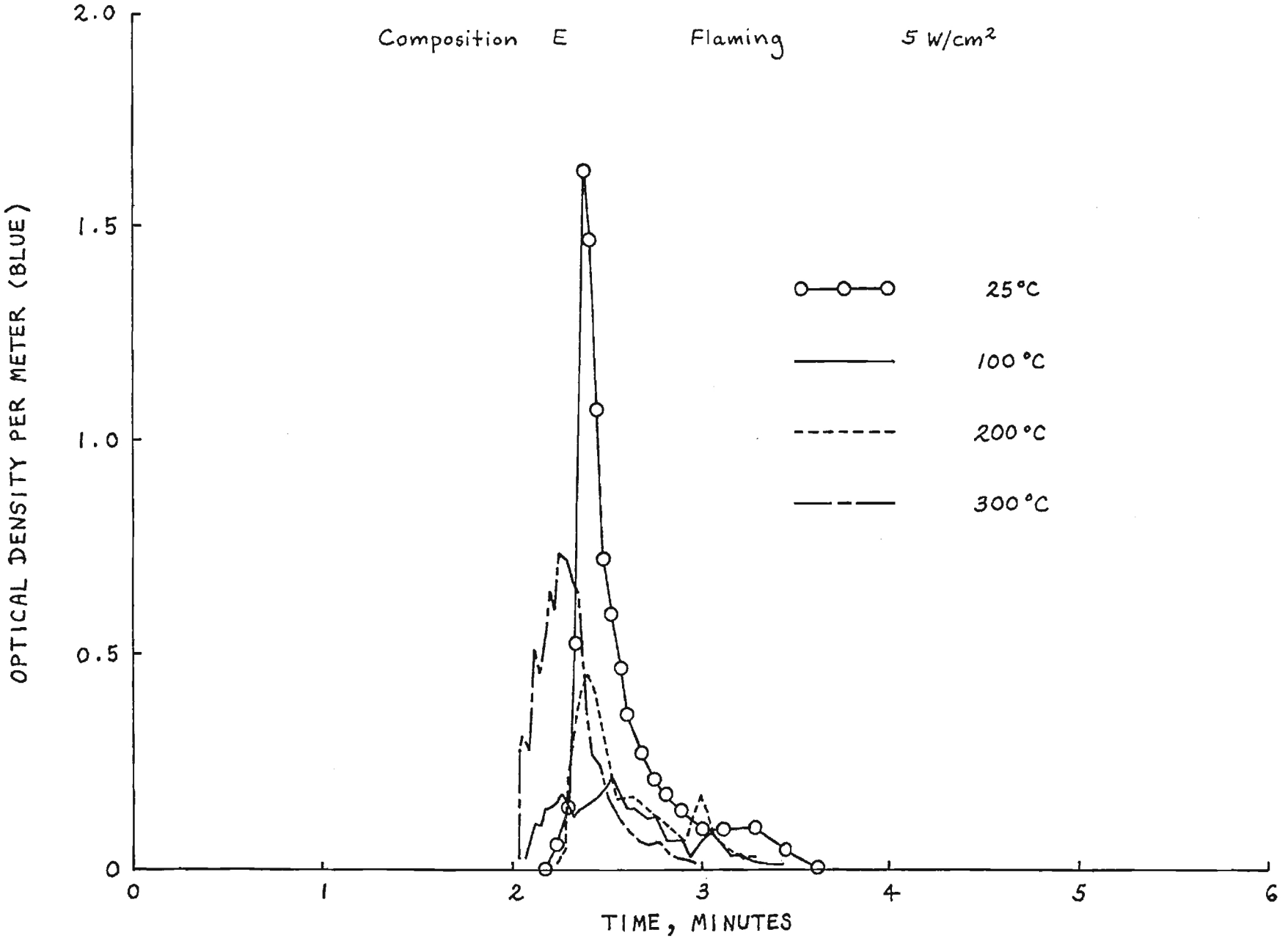


Figure 38. Smoke Optical Density Behavior under Different Temperature Conditions - Flaming Polyurethane

Summary

In flaming tests of five flexible urethane foams, sample weight loss measurements show a slight increase in burning rates as environmental temperature is increased. Also, fire retardant additives did not significantly affect the rate at which the sample burned (for the conditions studied). Time resolved mean particle size measurements show that larger particles are generated as the environmental temperature increases, but that there are few differences in particle sizes among the five samples tested. In room temperature tests, Composition A produced considerably lower optical densities than the other fire retarded samples, however measured optical densities were near the same levels for all samples in tests at higher temperatures. Differences are observed in particle size and optical density behavior between flaming and nonflaming conditions.

VI. RESULTS OF TESTS OF FLEXIBLE URETHANE SAMPLE GM23 - PHYSICAL PROPERTIES DATA

Room temperature tests have been conducted in order to make an initial determination of the characteristics of smoke produced during flaming and nonflaming combustion of Products Research Committee sample bank material GM23. The samples were mounted in the vertical position and the CPTC ventilation gas was composed of air flowing at 425 liters per minute. Sample dimensions are 75 mm x 75 mm (exposed surface) x approximately 15 mm thick; corresponding to sample weights of about 3.3 grams. During both tests, the sample surface was exposed to 5 W/cm^2 radiant flux, where a propane pilot burner was utilized to ignite the sample in the flaming test.

Weight loss data for Sample GM23 is presented for both nonflaming and flaming cases in Figure 39. These data show that the weight loss under flaming conditions is much more rapid than the weight loss in the nonflaming test. Also, this sample leaves a considerable fraction of the original sample in the form of char which remains in the sample holder.

The smoke particle size distribution obtained with the cascade impactor for the nonflaming case is given in Figure 40. These data show that the particle sizes measured for GM23 are comparable to the particle sizes measured for five other flexible urethane foams (see Chapter II). However, the relative amount of smoke (by mass) produced by this sample is somewhat less than the smoke generated by the other flexible urethane samples tested in this program. The characteristics of smoke produced by sample GM23 under flaming conditions prevented accurate measurement of size distribution in the flaming test.

Figures 41 and 42 provide time histories of the mean particle diameters (41) and the smoke optical densities (42) for both the flaming and nonflaming tests of sample GM23. The particle size data show that in room temperature

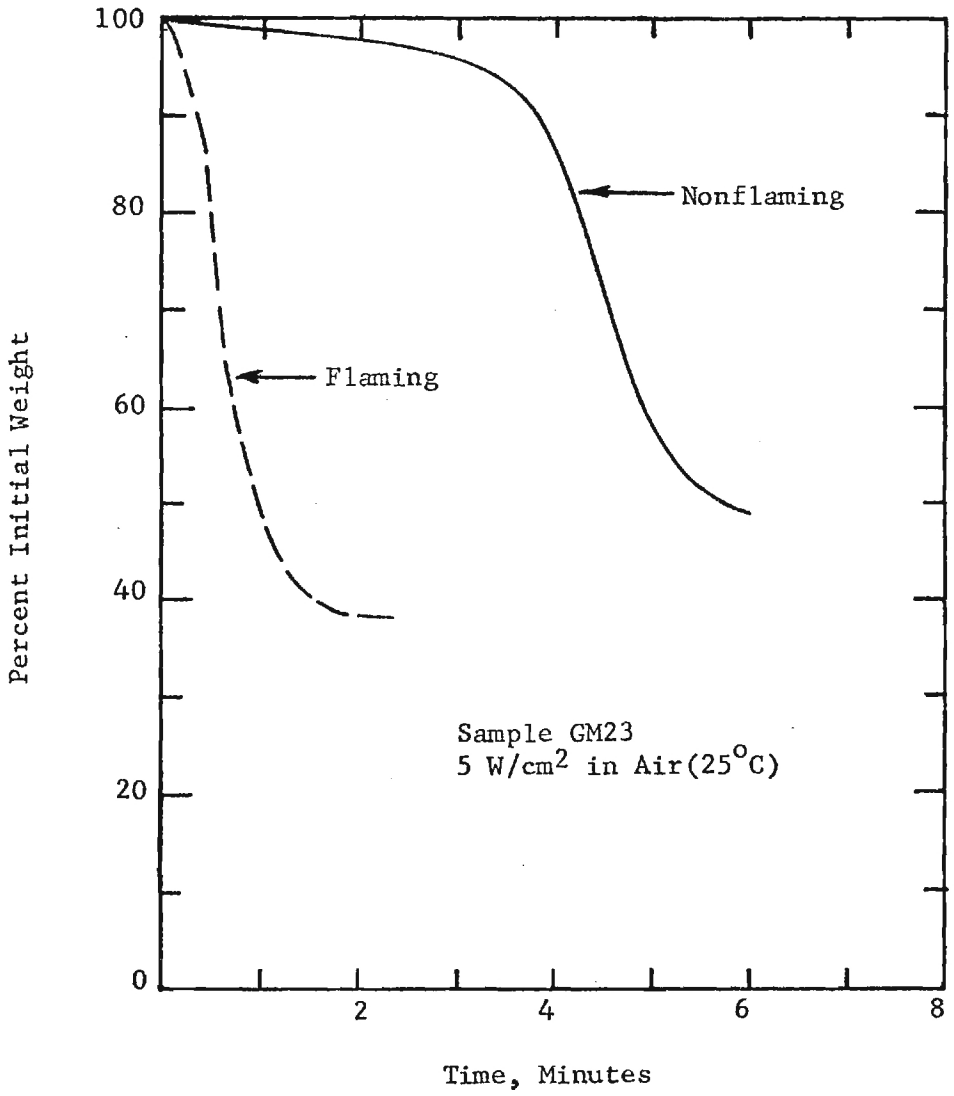


Figure 39. Weight Loss of Polyurethane Sample GM23 under Flaming and Nonflaming Conditions in Room Temperature Air

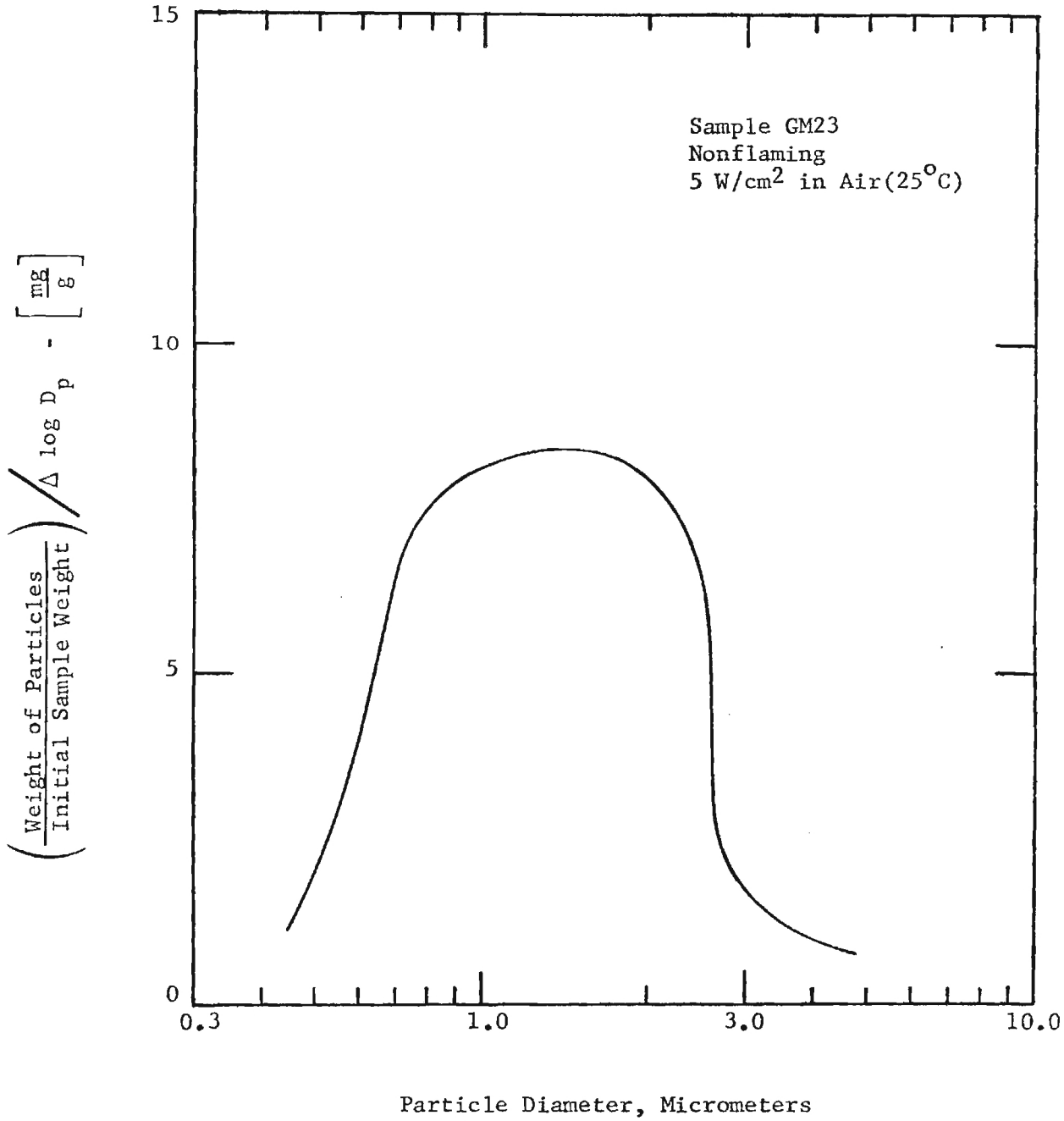


Figure 40. Integrated Smoke Particle Size Distribution for Polyurethane Sample GM23 - Nonflaming Conditions at 5 W/cm^2 in Air(25°C)

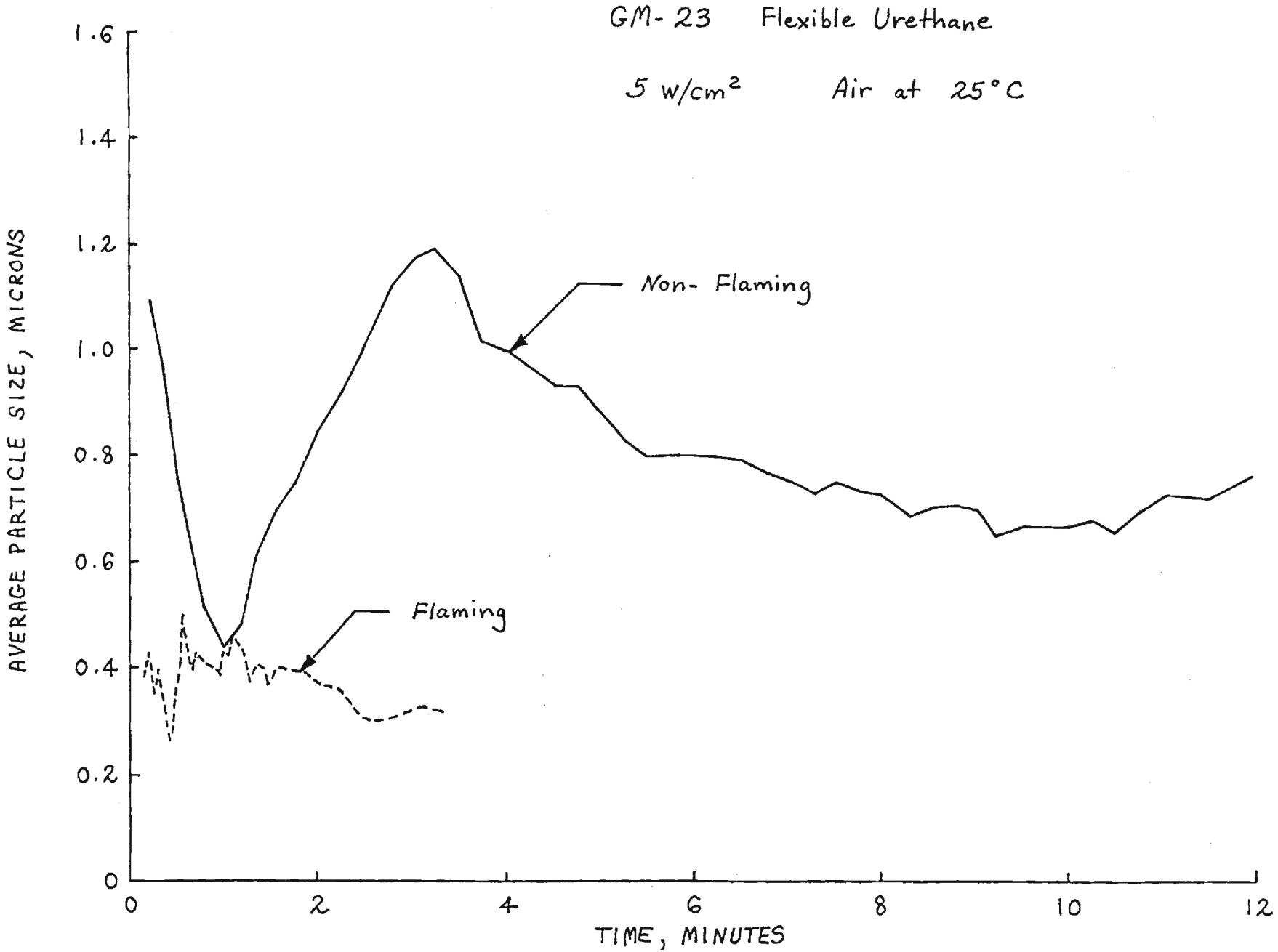


Figure 41. Time Resolved Smoke Particle Size Behavior for Polyurethane Sample GM23 under Flaming and Nonflaming Conditions in Room Temperature Air

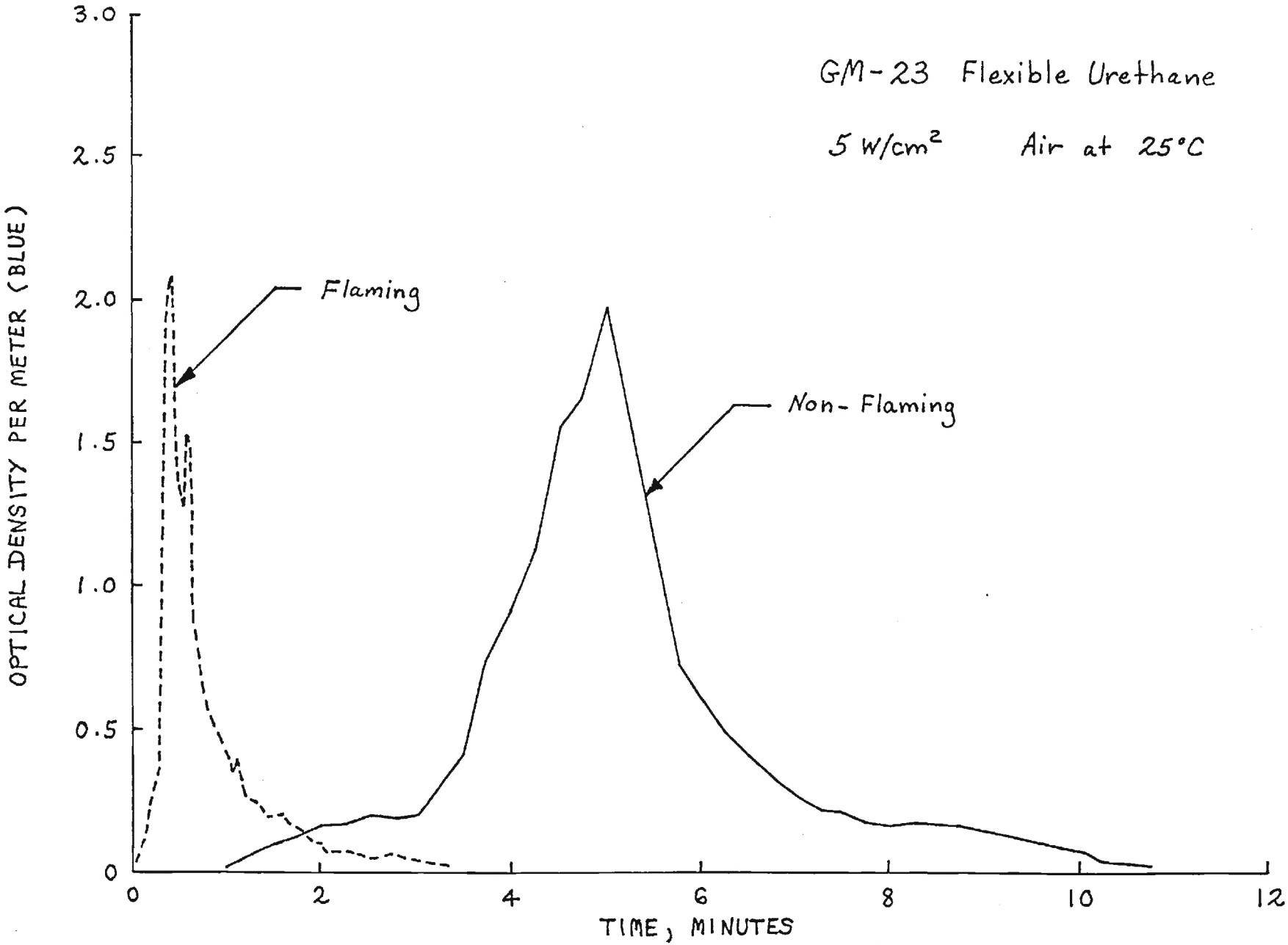


Figure 42. Smoke Optical Density Behavior for Polyurethane Sample GM23 under Flaming and Nonflaming Conditions in Room Temperature Air

tests, the particle sizes are considerably smaller under flaming conditions when compared to nonflaming conditions. On the other hand, maximum optical densities (Figure 42) are nearly the same in magnitude, although the smoke density peaks earlier and drops off faster in the flaming case. These data are consistent with the data obtained for the four fire-retarded flexible urethane compositions (of known composition) presented in Chapters IV and V.

VII. CHEMICAL ANALYSIS OF URETHANE SMOKE PARTICULATES

Chemical analysis of the particulates generated from the combustion of polyurethane samples under nonflaming conditions has been carried out with two primary objectives: (1) the identification of compounds with known high toxicity and (2) the identification of compounds important in determining the mechanisms of smoke formation. In the first category, compounds of prime interest have been low molecular weight compounds known to possess acute toxicity (such as HCN and acrolein) which are likely to be adsorbed onto the smoke particulates. Work in this area is in the preliminary phase, but the general analytical scheme under development involves the thermal desorption of these compounds from the particulates in a stream of dry N_2, collection and concentration of these compounds with a packed trap and subsequent release of the volatile components for analysis by gas chromatography. Identification is by GC retention time and by GC/MS. Methodology is currently under development for quantitation of this analysis, and recovery experiments using standard atmospheres of certain known mixtures are underway.

In the second category, the emphasis has been on obtaining thorough preseparation of the complex particulate material prior to the analytical step, in order to obtain reliable compound identification. Considerable progress has been made in this direction in the analysis of the high molecular weight compounds found in the particulates. However, the very complex nature of the organic mixture and the very similar nature of many of the compounds, such as the presence of mixtures of isomers or of the members of homologous series, has made separation and identification of polyurethane particulates a difficult task.

A. Analytical Procedure for Polyurethane Particulates

The procedure used for clean-up and identification of polyurethane particulates was as follows: After an alkali wash, the remaining neutral and basic components were dissolved in CH_2Cl_2, then the solution dried and concentrated carefully to avoid possible loss by evaporation of lower boiling components.

The FID gas chromatograms of two typical flexible polyurethane foam samples (Compositions A and B) are shown in Figures 43 and 44. It can be seen that adequate separation is achieved without the need for prior preparative high pressure liquid chromatographic work. It is also apparent that the traces for the samples are remarkedly similar, differing only in minor details. In addition, there is a recurrent pattern of major doublet peaks, flanked by satellite peaks, which repeats across the chromatogram. This is indicative of the presence of homologous series of isomeric compounds.

In an attempt to identify the particulate components by GC/MS,total ion and single ion chromatograms were made. Also mass spectra of individual peaks eluted from the GC were recorded and compared with mass spectral reference data stored in the Aldermaston computer files. The total ion chromatogram of polyurethane Composition A (FRN No. 6000) (Figure 45) shows a number of quite well resolved peaks. However, single ion chromatograms at M^+/e 44, 59 and 87 show the presence of these ions in virtually every chromatographic peak. Similarly, mass spectra of typical individual peaks from the chromatograph (as indicated in Figure 45) show very similar fragmentation patterns. Peaks (a) (Figure 46); (b) (Figure 47); (c)(Figure 48) and (d)(Figure 49) are too much alike to allow any positive identification from the mass spectral data alone.

Total ion chromatograms from additional polyurethane samples were strikingly similar to the one in Figure 45 (FRN No. 6000). The total ion chromatogram

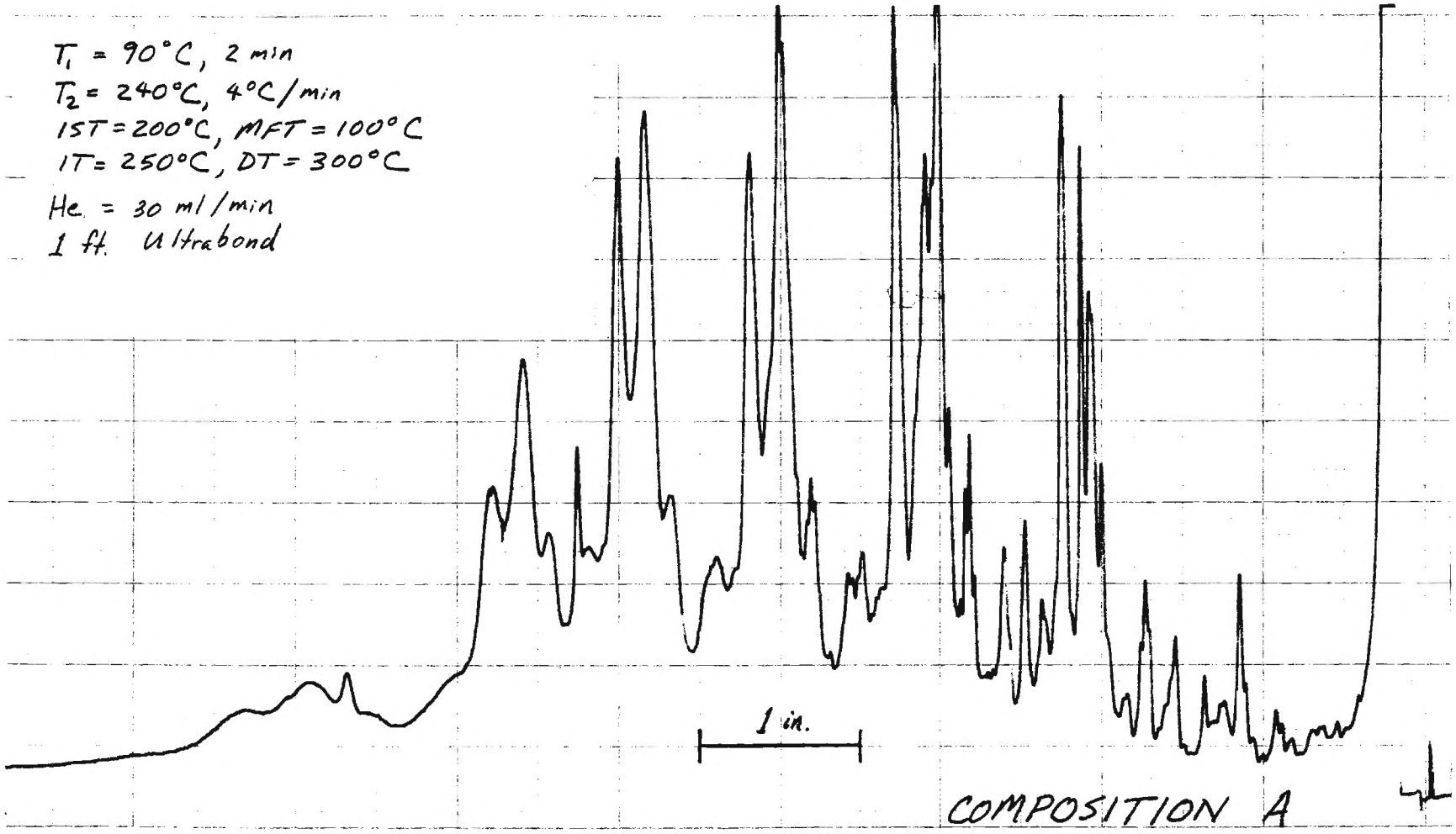


Figure 43. Gas Chromatographic Separation of Polyurethane Smoke Particulates - Composition A.

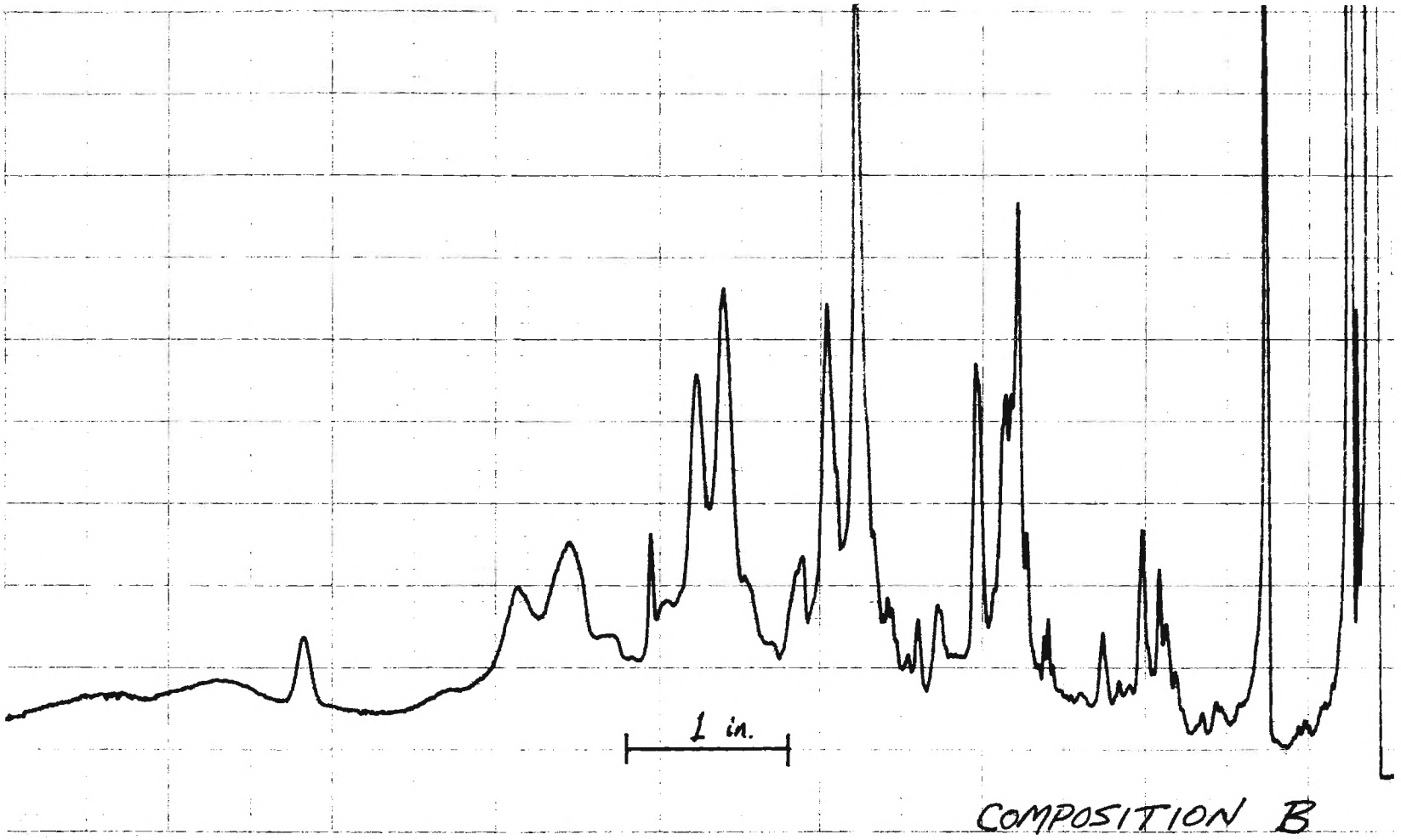


Figure 44. Gas Chromatographic Separation of Polyurethane Smoke Particulates.

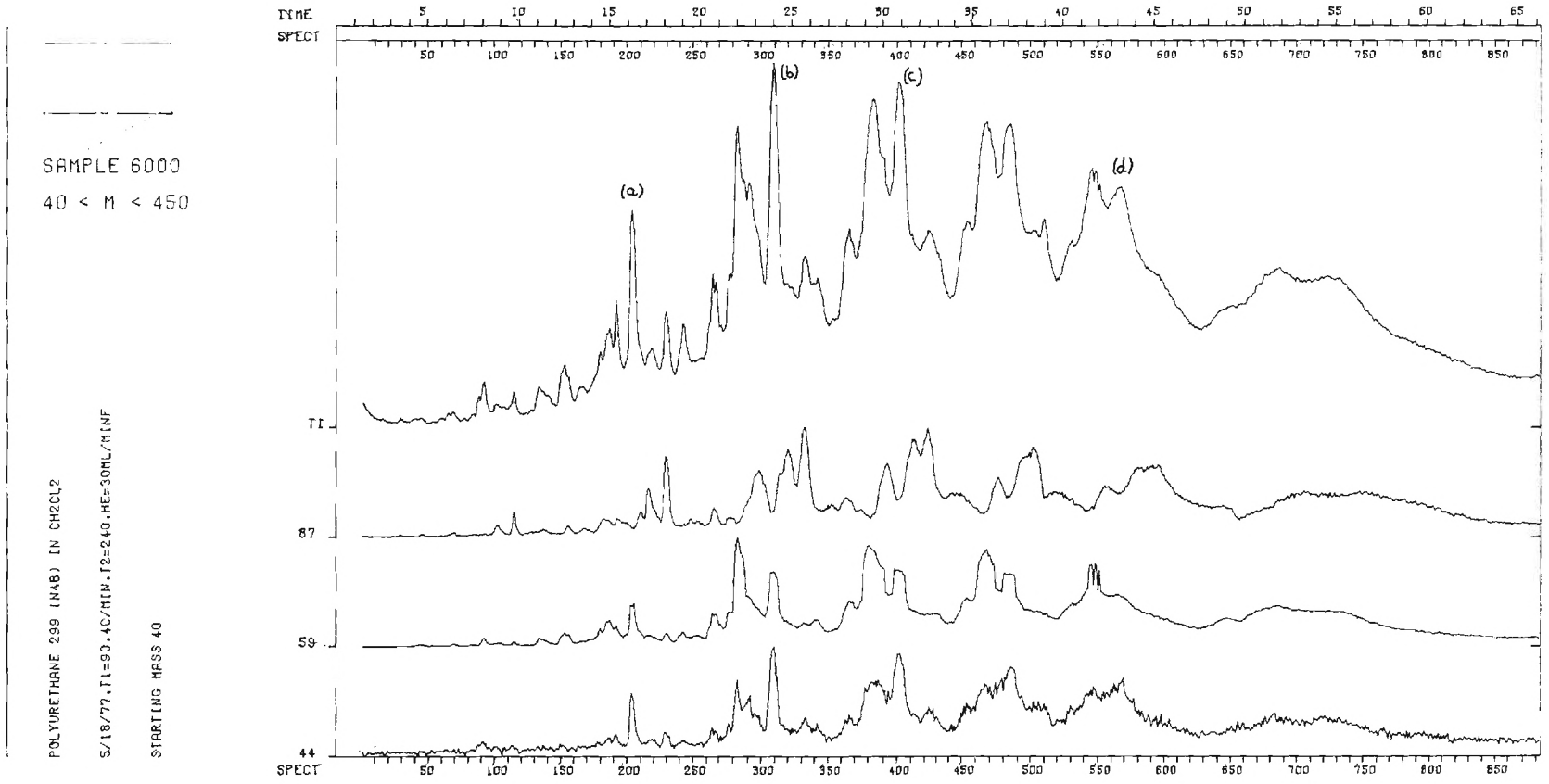


Figure 45. Single and Total Ion Chromatograms for Polyurethane Smoke Particulates

Figure 46. Mass Spectrum of Single Gas Chromatographic Peak for Sample FRN No. 6000.

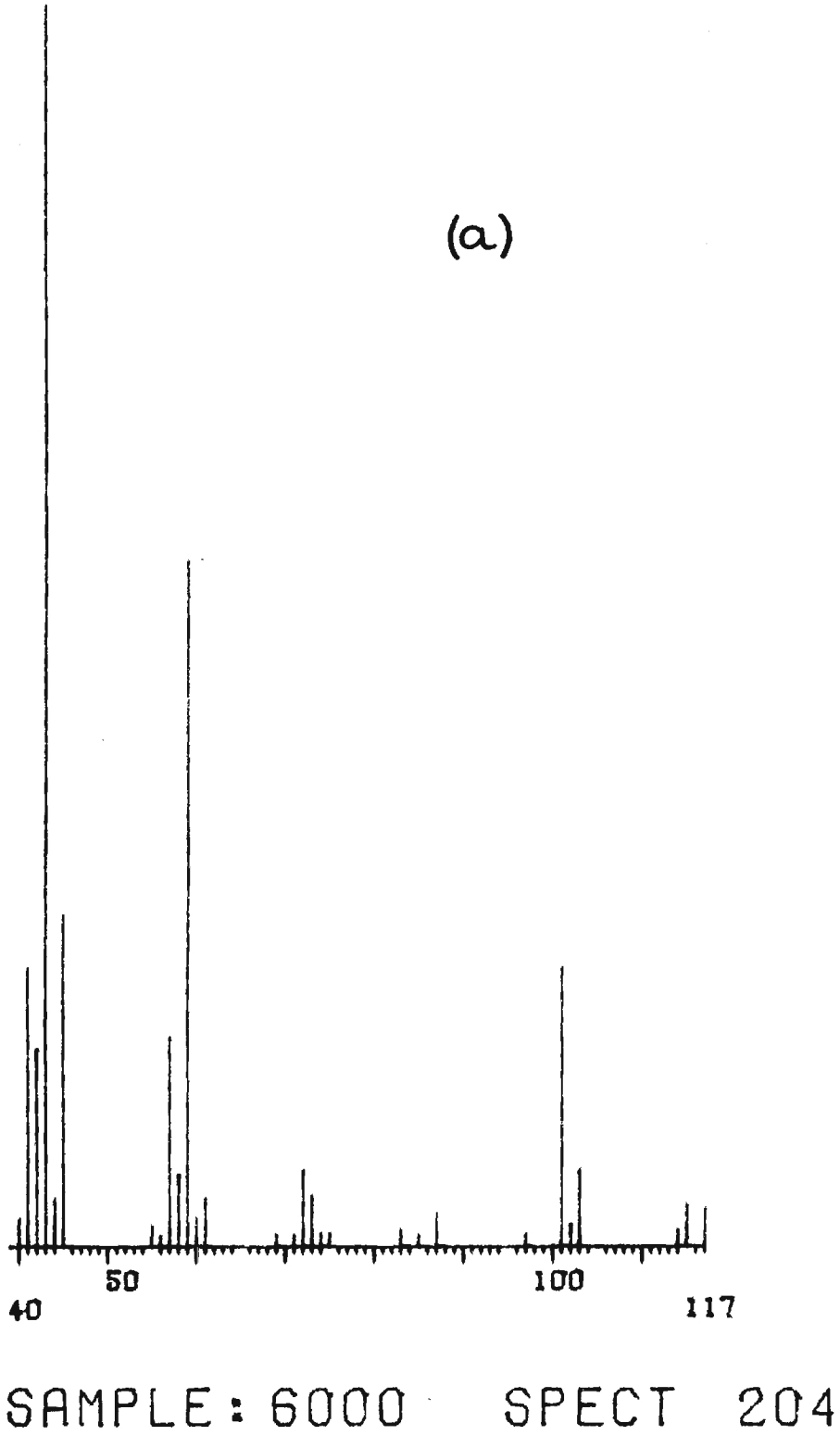


Figure 47. Mass Spectrum of Single Gas Chromatographic Peak for Sample FRN No. 6000.

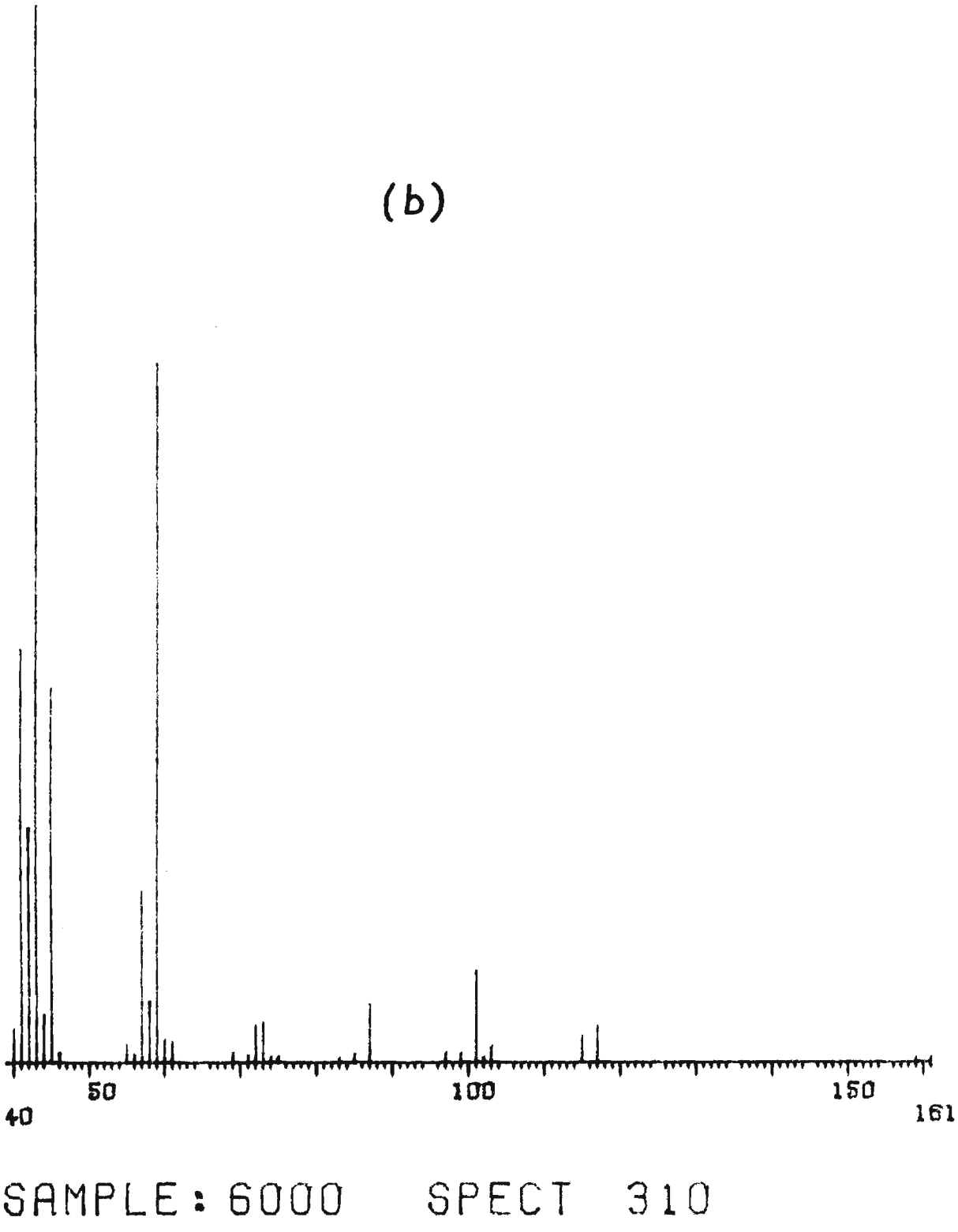


Figure 48. Mass Spectrum of Single Gas Chromatographic Peak for Sample No. 6000.

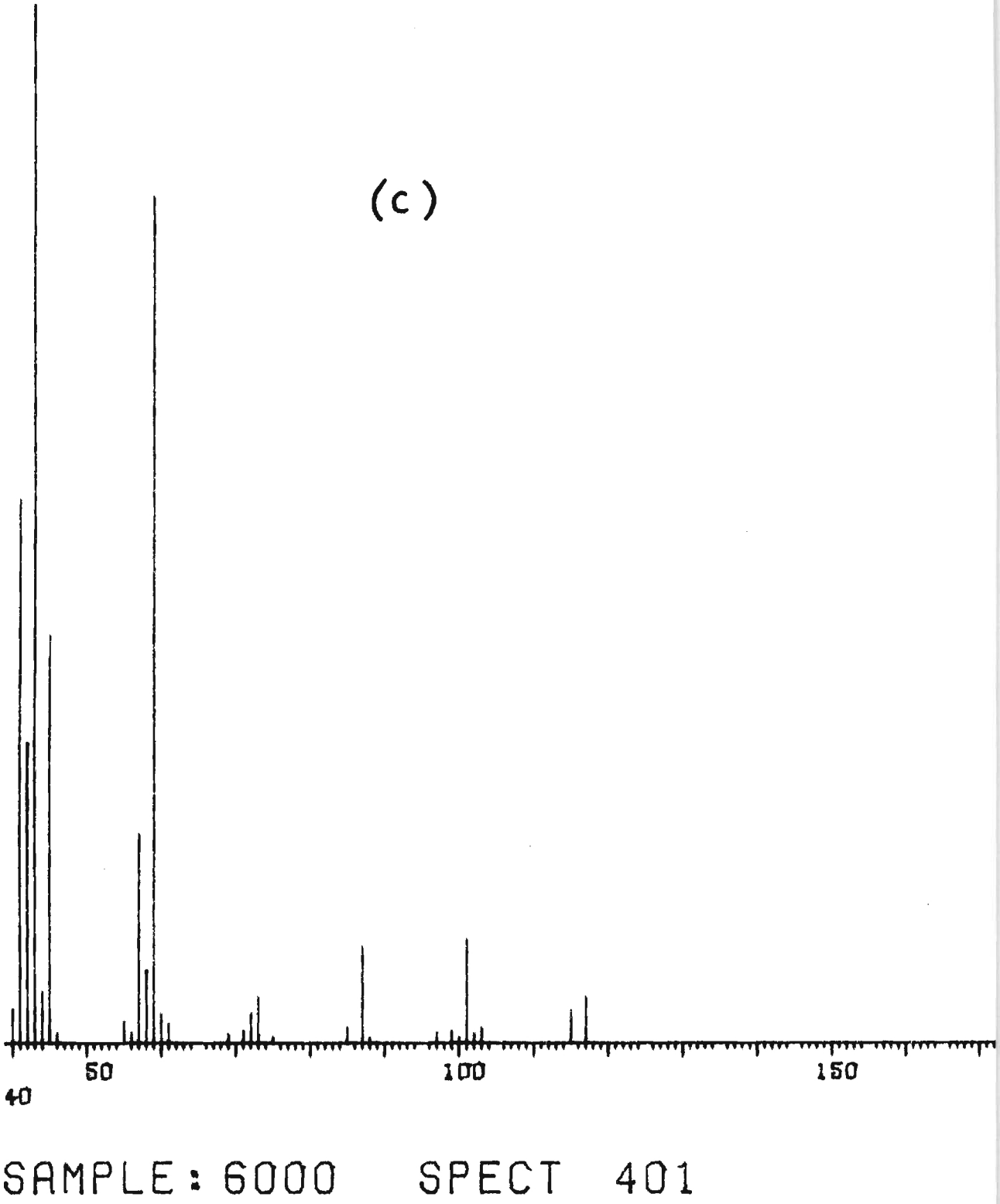
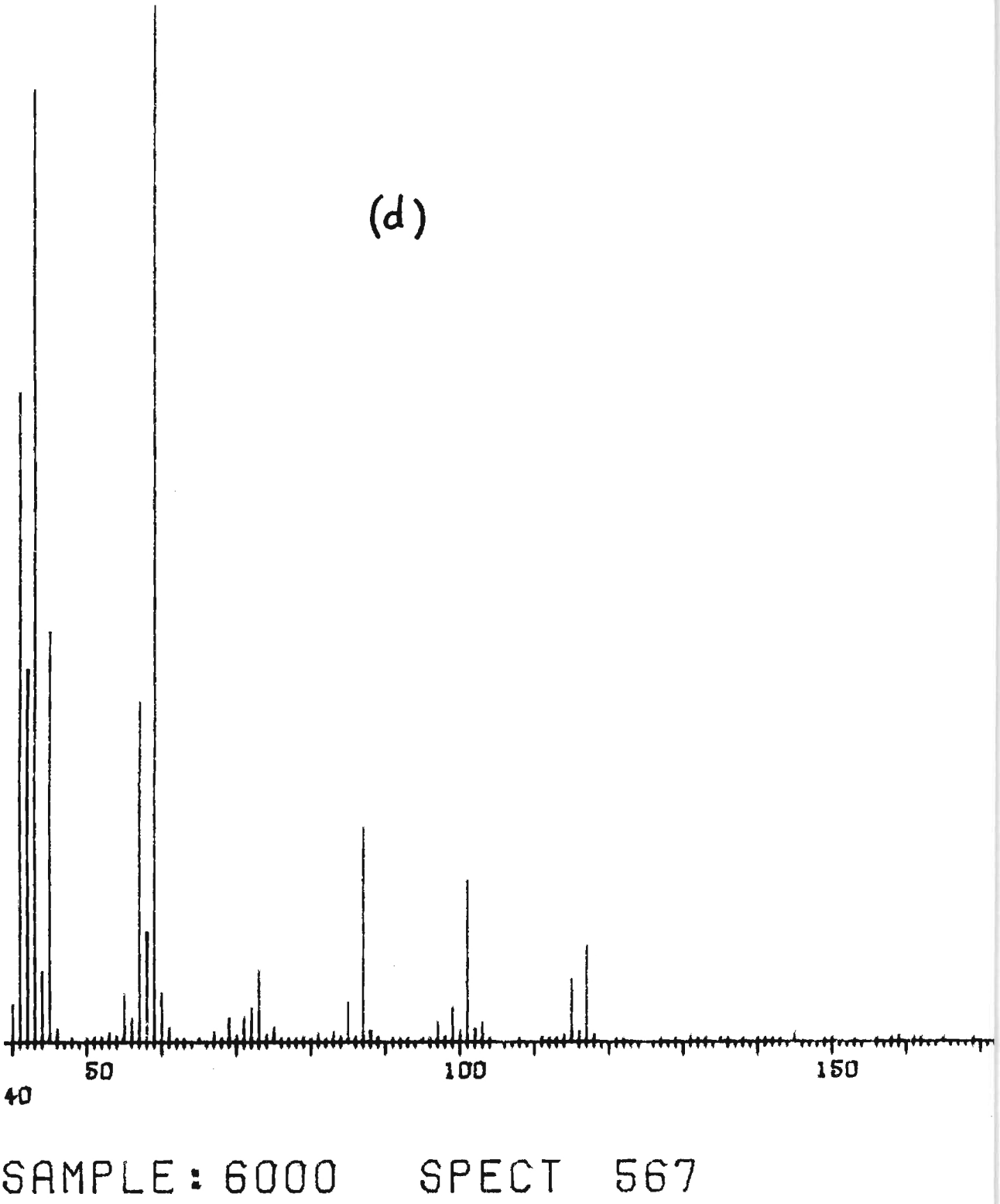


Figure 49. Mass Spectrum of Single Gas Chromatographic Peak for Sample No. 6000.



for sample FRN No. 6002 is illustrated here (Figure 50). In an attempt to produce as many dissimilar fragmentation patterns as possible, and also conceivably a recognizable parent ion, these mass spectra were recorded at the low electron impact acceleration voltage of 14 eV, compared to the 70 eV used for FRN No. 6000. It is clear from this data that chemical ionization will be necessary in order to obtain recognizable characteristic mass spectra. For this reason, a chemical ionization system will be added to the mass spectrometer during the coming year, and this should result in superior identification of the components of the polyurethane particulates. In addition, ultra-violet and infrared absorption spectra will be used as back-up techniques, to supplement the characterization by GC/MS.

B. Conclusions

Very good separation of the components of the smoke particulates from polyurethane combustion has been achieved. It is anticipated that in the near future positive identification of these components will be possible, at which stage quantitative data will be obtained which correlates ratios of individual compounds with the precise composition of the polyurethane foam. Also, quantitative data on toxic components adsorbed onto the particulates will be determined.

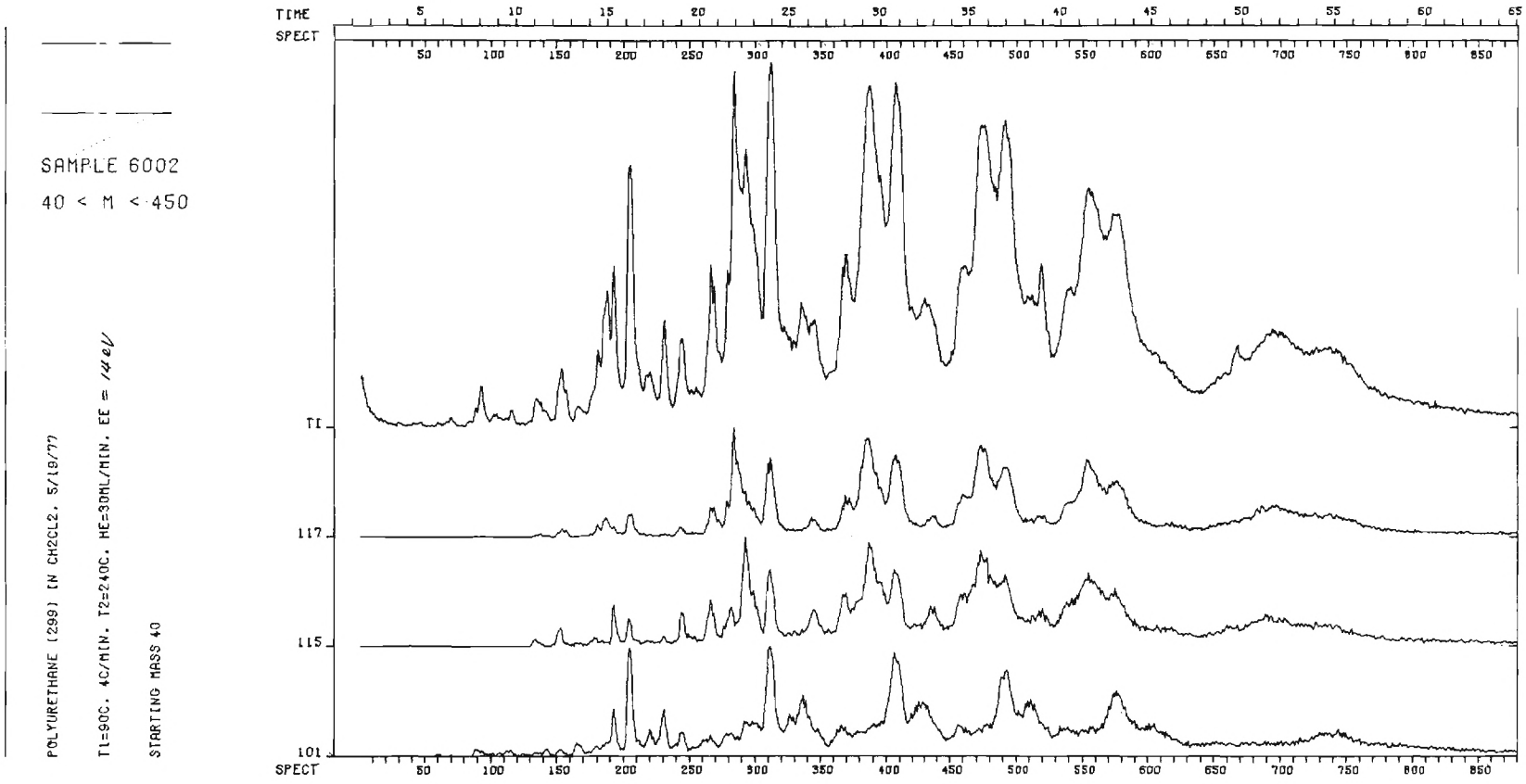


Figure 50. Single and Total Ion Chromatograms for Polyurethane Smoke Particulates

VIII. REFERENCES

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